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The Lysimeter Concept

Environmental Behavior of Pesticides

EDITED BY
F. Führ, R. J. Hance, J. R. Plimmer, and
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Foreword

THE ACS SYMPOSIUM SERIES was first published in 1974 to provide a mechanism for publishing symposia quickly in book form. The purpose of the series is to publish timely, comprehensive books developed from ACS sponsored symposia based on current scientific research. Occasionally, books are developed from symposia sponsored by other organizations when the topic is of keen interest to the chemistry audience.

Before agreeing to publish a book, the proposed table of contents is reviewed for appropriate and comprehensive coverage and for interest to the audience. Some papers may be excluded in order to better focus the book; others may be added to provide comprehensiveness. When appropriate, overview or introductory chapters are added. Drafts of chapters are peer-reviewed prior to final acceptance or rejection, and manuscripts are prepared in camera-ready format.

As a rule, only original research papers and original review papers are included in the volumes. Verbatim reproductions of previously published papers are not accepted.

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Preface

The actual global area of agricultural land is approximately 1.4 billion ha. The world population will increase from 6 to at least 8–9 billion during the next 25 years. Every year, about 1% of the land used for agriculture is lost as a result of erosion, salinization, overuse and, in particular, urban development. So, as has been predicted by Nobel Prize winner Norman Borlaug, the increasing food and feed supply must be produced on land already in use. This means that agriculture must do everything possible to grow plants under conditions that will permit them to attain their inherent yield potential. To implement sustainable development means using integrated plant management that incorporates the most appropriate use of chemicals in the form of fertilizers as well as the use of pesticides to reduce yield losses and stabilize production. Integrated crop management is a dynamic system that is constantly being further developed to make efficient and sensible use of the latest research and technology.

Despite the present use of plant protection, 40% of the potential yield of the eight most important world crops are still lost to diseases, insect attack, and weed competition. Therefore, we must use modern pesticides more effectively by delivering the active ingredient to the place where it is needed at the right time and at the required concentration. In addition, because all chemicals applied finally reach the soil, we must know beforehand whether this creates any possible risk to the environment. The lysimeter concept can contribute to all these aims by allowing the application of radiolabelled pesticides in accordance with good agricultural practice.

Lysimeters have been utilized to study the long-term behavior of radiolabelled pesticides in agroecosystems for some 25 years. The lysimeters contain soil monoliths—blocks of undisturbed soil. Several laboratories have contributed to understanding the fate of pesticides in the environment and their performance in the plant–soil system. The combination of lysimeter experiments with detailed complementary studies has added considerably to current knowledge of the environmental behavior of pesticides. In addition, this information opens new possibilities of gaining further information to improve the pesticide

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use by studying their route of entry into plants and soils, evaluating new formulation approaches that will reduce the quantity of unused residues that may affect non-target organisms. This objective can only be completely realized through multilateral interdisciplinary cooperation. All leading companies still engaged in pesticide research and development now have lysimeter facilities available, and no new compound that will not have been tested in a lysimeter experiment at an early stage of development will be introduced into the market.

On the other hand, pesticide regulatory agencies will increasingly use lysimeter data in combination with data from standardized detailed studies, as the standard set for information. In Europe, the regulatory agencies have now included the lysimeter experiment in the procedures used for assessing the long-term behavior of pesticides in a representative agricultural ecosystem, especially their leaching behavior. But the lysimeter experiment is not just an aged leaching test under outdoor conditions because it offers a real opportunity to conduct a complete study of environmental behavior of pesticides in the soil–water–plant system. The addition of a wind-tunnel erected on the top of the lysimeter also makes it possible to obtain information on volatilization and biomineralization.

The presentation of the International Award for Research in Agrochemicals sponsored by American Cyanamid (Princeton, New Jersey) provided the opportunity to present the lysimeter concept in an Award Symposium. One major goal of this book is to intensify communication and cooperation among agriculture, industry, and government to improve confidence that research on future plant protection products will assure their proper use in accordance with present day knowledge and guarantee continued production of safe and high quality food at a low cost. In particular, knowledge gained by lysimeter experiments with radiolabelled pesticides should also stimulate discussions with scientists of all plant disciplines to improve integrated crop management including biological control.

The editors and authors of the contributions to this book are especially thankful to the American Chemical Society for providing the opportunity to present the lysimeter concept. In addition to the lectures presented at the Award Symposium on the occasion of the 213th Meeting of the American Chemical Society, Agrochemicals Division at San Francisco on April 14, 1997, chapters based on selected contributions to the poster session demonstrate clearly the special advantages of combining outdoor lysimeter experiments with detailed studies on plant uptake, volatilization–mineralization, leaching, and bound residues in soils and plants. The editors express their great appreciation for the constructive cooperation of the authors and for the reviews, suggestions, and assis-

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tance provided by so many in the development of this book. Special thanks are due to Joel Coats for his advice and assistance and to Martina Kreutzer for secretarial help.

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Chapter 1

Comprehensive Tracer Studies on the Environmental Behavior of Pesticides: The Lysimeter Concept

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The environmental behaviour of pesticides is investigated with ^{14}C-labelled active ingredients in lysimeter experiments simulating good agricultural practice. These microplots with an area of 0.5 to 1.0 m^2 and an undisturbed soil column of at least 1.1 m are taken from field sites representing different soil types. The ^{14}C-labelled compounds are applied as in agricultural practice to plants, seeds and soil. The results yield information about uptake and metabolism in plants, volatilization and mineralization, translocation in the soil and leaching and the status of residues in the soil. On the basis of radioactivity and mass balances, detailed studies are designed to contribute to the concept of studying the long-term behaviour of organic chemicals in the agroecosystem. The results can lead to practical recommendations for the improved use of pesticides in general, and they are now also used as part of the registration requirements. Since all leading companies engaged in pesticide development now have lysimeter stations available, no new compound will be introduced into the market without already having been tested in lysimeter experiments at an early stage of development. This chapter gives an introduction to the different contributions compiled in this volume.

The world population has doubled from 2.5 billion in 1950 to 5 billion in 1987. In the same time the yields of the major crops have been raised by more than 100 % as demonstrated for average wheat yields in Germany which, starting with less than 30 dt ha^{-1} in 1950, reached more than 70 dt in 1995. With 1950 standards, twice the acreage of 14 million km^2 would have to be used, equivalent to all the potential agricultural land of 28 million km^2, to feed the world population. All disciplines of agriculture have

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contributed to this extraordinary success, but at the same time farmers have experienced the most dramatic change in farming within just 2 to 3 decades. Modern technology has replaced ox and horse power as well as labour force. Harvesting of grain with combines became state of the art in the sixties, replacing binder and threshing machines, and hand weeding was replaced by herbicide use with the development of modern pesticides starting with 2,4-D, DDT and parathion in the forties. Their characteristics, among others, are that only a few kg ha^{-1}, and now even less than 100 g ha^{-1}, are used to control insects, fungus diseases and weed competition.

Fate of Pesticides in Agroecosystems

In 1974 on the occasion of the 3rd IUPAC Congress "Pesticide Chemistry", organized at Helsinki, Finland, residue analysis was still at the centre of interest as far as pesticide research was concerned. However, due to the intensive discussion which started in the mid-60's after the publication of Rachel Carson's book "Silent Spring" (1), research in the fields of mode of action, metabolism, and environmental behaviour of pesticides has developed into multilateral interdisciplinary cooperation, in which pesticide chemists cooperate with agricultural chemists, soil scientists, microbiologists and plant physiologists (2,3). All the processes which determine the fate of a pesticide in the soil-plant system (Figure 1) are of particular interest not only for industry, which invents and produces the active ingredients, and for the farmer, who uses them to produce a predictable, reliable and good-quality crop, but also for the regulatory authorities who are responsible to the consumer as well as to the user for safety according to the present state of knowledge (4).

In pesticide registration, besides efficacy and toxicology, the fate and effects of pesticides in ecosystems are of equal importance (4,5). Therefore the criteria for the assessment of pesticides in the registration procedure include volatility and behaviour in the air, fate in the soil, entry into the ground water, degradability and fate in the water/sediment system, bioaccumulation and side effects on aquatic organisms, soil microflora, earthworms, bees, birds and wild mammals and, last but not least, beneficial organisms, in order to meet the requirements of the German Plant Protection Act (6), which states in Article 15: "The plant protection substance, when used for its intended purpose and in the correct manner, or as a result of such use,

a) does not have any harmful effects on human and animal health or on *ground water*,

b) does not have any other effects, particularly with regard to the *natural balance*, which are not justifiable in the light of the present state of scientific knowledge."

Many governments have issued guidelines for the data they need to evaluate the environmental risk of a pesticide. The FAO guidelines (7) recommend a 4-step sequence of tests of increasing complexity ranging from standard laboratory tests on adsorption/desorption and leaching in soil and supplementary laboratory tests which include degradation in water and sediments, photolysis on soil surface and estimation of volatility, to simulated field and field trials, and finally post-registration monitoring.

Using standardized methods, degradation behaviour (8) including dissipation time and mineralization to carbon dioxide is studied, and also the leaching tendency,

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as well as possible side effects on key biological processes in the soil (4). An assessment of these results is the basis for regulations for the application of the pesticide, e.g. restrictions or prohibition in water catchment areas. Just 10 years ago, sophisticated detection methods led to pesticide residues being found with increasing frequency in soils, drainage and ground water (9,10). This led in particular to a more intensive consideration of the long-term behaviour of pesticides in agroecosystems (Figure 1).

The key to preventing a translocation of pesticides out of the topsoil into the subsoil is to be found in more precise knowledge of the binding, release, conversion and mineralization taking place in the soil after the intended use of pesticides. In addition, more intensive research must be undertaken to understand the movement of water and transport of residues within the soil, particularly the exchange between the topsoil region and the subsoil. Only labelling of the active ingredients, e.g. with the radioactive carbon isotope ^{14}C, enables (apart from an extreme reduction of the detection limits) the analysis of total residues in various soil layers, and above all, the quantification of the residues persisting in the soil in a bound form, not extractable and therefore not otherwise analytically detectable (11,12).

Many factors besides physicochemical properties of the compound such as mode and time of application, climatic parameters (temperature, moisture, aeration) and plant species and physiological differences interact in influencing the metabolism of the active substances, their further path into the plant, and the amount and type of residues in soil, the loss by runoff processes and translocation into subsoil regions and

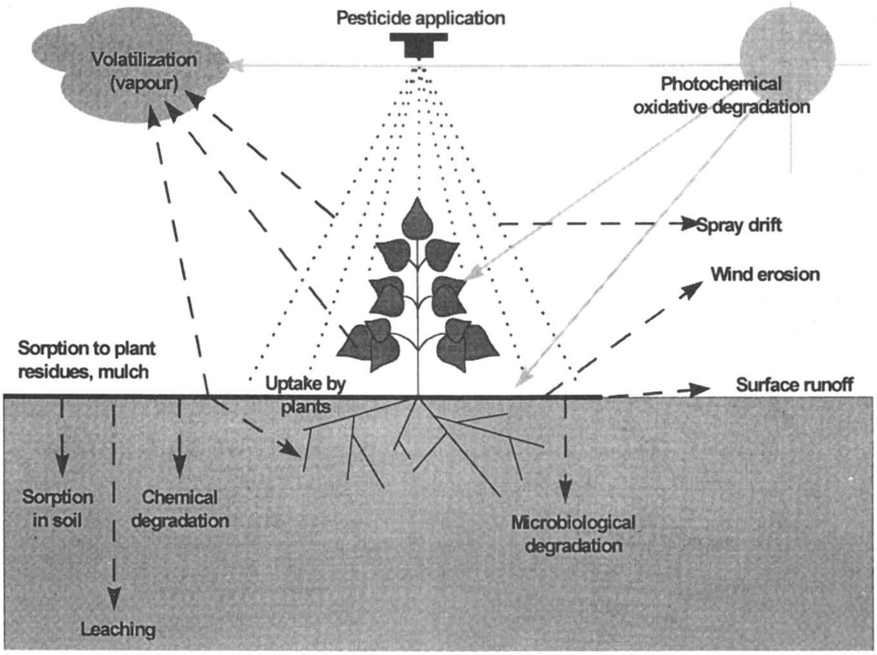
Pesticide application
Volatilization (vapour)
Photochemical oxidative degradation
Spray drift
Wind erosion
Sorption to plant residues, mulch
Uptake by plants
Surface runoff
Sorption in soil
Chemical degradation
Microbiological degradation
Leaching

Figure 1. The Fate of Pesticides in the Agroecosystem.

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possibly the ground water (Figure 1). For each pesticide, a different situation has to be considered, since besides physicochemical properties and formulation, especially the mode of application - the compound may be applied as a seed dressing or as a spray application either pre- or post-emergence or directly onto the growing plants - has the greatest influence on its environmental fate (3, 13, 14). Drift and condensation as well as washoff or runoff can drastically change the distribution pattern on a micro- as well as on a macroscale. Due to photochemical, chemical and biological degradation and sorption, fixation and binding processes (Figure 1), the bioavailable portion of the applied pesticide decreases immediately after application (13, 14). Plant growth and translocation in the soil lead to further dilution of residues in the soil-plant system. Finally, detection of the gaseous losses is also necessary for compiling an overall mass balance (15, 16).

The soil is the final sink for most of the pesticides. The processes of degradation, mineralization, adsorption and fixation, as well as translocation (Figure 1), are dependent on a number of soil properties such as texture, clay minerals, humic substance contents, pH value and nutrient as well as biological parameters such as microbial biomass and the species composition, especially in the rhizosphere, together with plant residues as a source of energy for microorganism populations (17). Terrestrial ecosystems are characterized by variable daily change in temperature and moisture, high contents of reactive surfaces, as well as an extremely wide range of species and population fluctuations of the microorganisms. They are largely subjected to aerobic conditions in the various microcompartments, but nevertheless also experience anaerobic conditions from time to time (18). It thus becomes clear that a prediction of the long-term behaviour of pesticides in an agroecosystem is only possible to a limited extent with the aid of results from standardized degradation, leaching and bioactivity (7) studies. It also has to be taken into consideration that each chemical has its own route of entry which decisively determines its environmental fate in the respective ecosystem.

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Test Systems

Field Experiments. Field trials are already conducted at an early stage of pesticide development to study the effectiveness of the pesticide action as far as its intended use is concerned. In addition, the guidelines now require field trials especially for relatively persistent or mobile compounds to supplement data from laboratory tests (5). However, in the field the many factors which effectively govern the fate of pesticides vary considerably so that finally each experiment represents a unique and nonrepeatable scenario. The full-scale field experimentation which would be necessary involves its own problems and limitations (19). Especially interactions between soil type and climate cannot be studied with incremental variations except by comparing results at the same site from different years or seasons (15). So, in conclusion, in order to obtain reliable estimates of pesticide behaviour in the field, a large number of replications at many sites representing different soil and climate conditions are required. But above all, the data just yield information on the detectable portion of a pesticide or its major metabolites, since only in a few countries is the use of ^{14}C-labelled pesticides allowed on the field scale. Especially in investigating the fate of low-rate chemicals such as sulphonyl urea compounds where just a few g a.i. ha^{-1} are applied, residues cannot be detected without using radiolabelling (20).

Lysimeter Systems. Lysimeters were already used in the 19th century for comprehensive research into the nutrient budget. The beginnings of lysimetry go back as far as 1688 (21). The word "lysimeter" originates from the Greek linking "lyo"(I dissolve) with "metron" (the measure, to measure). It is therefore a methodological instrument to study the fluxes of soil water and the substances dissolved in it. At the same time a balance of the nutrient budget in the soil can be established. For this purpose, the soils were mainly placed in the lysimeter in layers so that undisturbed soil profiles were only retained in a few cases. The largest of these facilities was set up in the summer of 1927 at the BASF agricultural experimental station in Limburgerhof (22). On 232 plots, numerous studies were performed on water balance and nutrient utilization as an accompaniment to intensive practice-oriented fertilizer research. A comprehensive description of lysimetry was made already by Kohnke et al. (23), and a bibliography on lysimeter experiments was compiled in 1984 by BASF (24). This list comprises 1800 citations, of which, however, only about 20 are concerned with issues from pesticide research.

Starting in 1972, the Institute of Radioagronomy of the Nuclear Research Centre Jülich has developed, in close cooperation with pesticide scientists from Bayer AG, Leverkusen, a lysimeter agroecosystem approach (2). Lysimeters have a number of features which give them obvious advantages over other experimental systems. First of all they almost exactly reproduce the environmental conditions that occur in the corresponding field soil (25). Soils from different representative field plots can be grouped at the same site and so exposed to the same climates. Secondly, radiolabelled compounds can be used which offer a combination of conventional analytical techniques with different tracer detection techniques (Figure 2), as will be demonstrated below.

Lysimetry at the Institute of Radioagronomy. At first 1-m^2 lysimeters packed with 0.45 m plough layer soil were used (26) since the essential processes responsible for the fate of pesticides mainly take place in the tilled soil layer. In addition to this, since 1974 soil monoliths with an undisturbed profile and a depth of up to 80 cm and cultivated surface areas of 0.25 - 0.5 m^2 have also been included in the studies (27).

Since 1983 undisturbed soil monoliths with a profile depth of 1.10 m have been available, removed from the field with the aid of stainless steel cylinders and inserted in stainless steel containers firmly embedded in the soil (Figure 2). More details are given by Steffens et al. (27). These lysimeters with a cultivated area of 0.5 or 1.0 m^2 are surrounded by control areas cultivated with the same crop. The experiments with ^{14}C-labelled pesticides are conducted in accordance with good agricultural practice. Fertilization and complementary plant protection measures are closely coordinated with agricultural practice. Natural precipitation as well as soil/air temperature and air humidity and soil moisture in different soil layers are recorded continuously (Figure 3). Soil moisture measurements are performed with time domain reflectometry (TDR). In addition, an access tube is installed centrally in some round 1.0-m^2 lysime-

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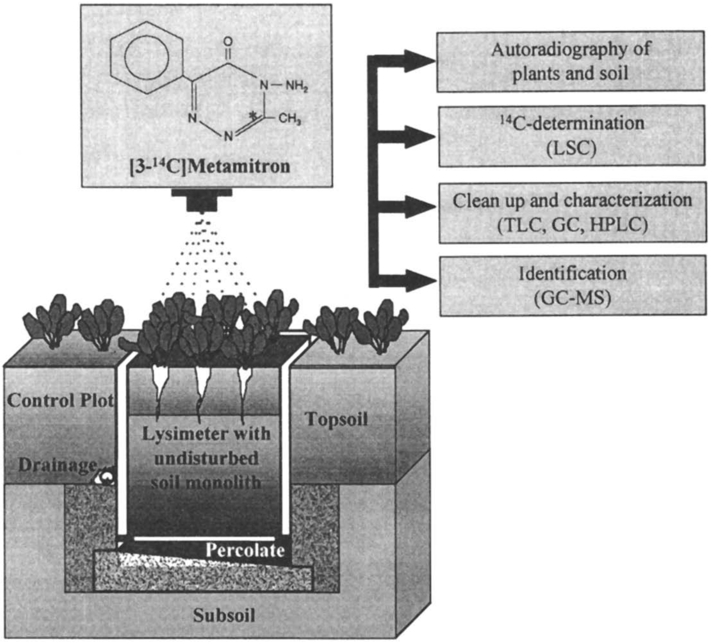
[3-^{14}C]Metamitron
N–NH$_2$
CH$_3$
Autoradiography of plants and soil
^{14}C-determination (LSC)
Clean up and characterization (TLC, GC, HPLC)
Identification (GC-MS)
Control Plot
Drainage
Lysimeter with undisturbed soil monolith
Topsoil
Percolate
Subsoil

Figure 2. The Use of ^{14}C-Labelling in Lysimeter Experiments - Cross Section through the Lysimeter Facility at the Research Centre Jülich.

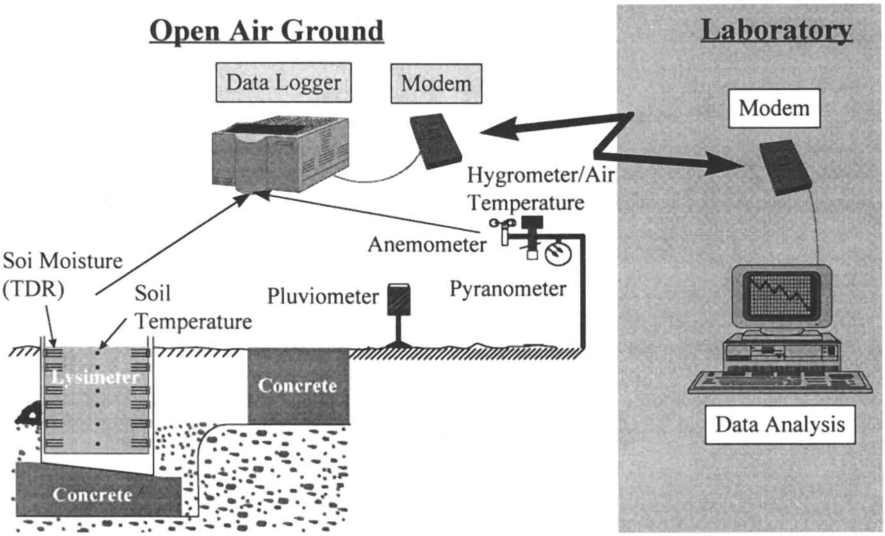
Open Air Ground
Laboratory
Data Logger
Modem
Modem
Hygrometer/Air Temperature
Anemometer
Soi Moisture (TDR)
Soil Temperature
Pluviometer
Pyranometer
Lysimeter
Concrete
Concrete
Data Analysis

Figure 3. Measurement and Registration of Climatic and Soil Parameters.

ters to discontinuously measure soil moisture in the soil profile with a neutron probe. Soil solution can be withdrawn via suction candles (25).

Fifty lysimeters (20 of 0.5 and 30 of 1.0 m^2 cultivated area) located on an area of about 2500 m^2 and distributed between 10 plots of 5 lysimeters each are now available for investigations of the long-term behaviour of pesticides in the agroecosystem.

ters to discontinuously measure soil moisture in the soil profile with a neutron probe. Soil solution can be withdrawn via suction candles (25).

The Institute's many years of experience in this research sector (2, 11, 26-28) were of great advantage in constructing the station. The soil used for the experiments is removed from a 7.5-ha field. This soil is an orthic luvisol (Parabraunerde), a clayey silt derived from loess widespread in the Federal Republic of Germany, and represents a fertile soil mainly used for agriculture. A second arable soil, a sandy soil (gleyic cambisol), is also available in order to include a more water-permeable soil type in the experimental programme, particularly for questions of the leaching behaviour of pesticides (29).

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Application of ^{14}C-labelled Pesticides. In agricultural practice, sprayed solutions of pesticides are assumed to be applied evenly. On microplots like lysimeters, with an area of 0.5-1.0 m^2, homogeneous spraying is rather difficult. However, a homogeneous distribution of a pesticide solution on plants and soil is a prerequisite in lysimeter experiments for sampling reasons. Realistic rates of pesticides and spray solution volumes (20-40 ml m^{-2}), commonly used in agricultural practice, should be applied to give results transferable to the field situation. Two different spraying techniques are used: a hand-operated garden sprayer and a special semiautomatic sprayer with nozzles used in agricultural practice which guarantees a practice-like application (droplet spectrum, application volume) in combination with a very homogeneous distribution onto the target surface (30).

Before spraying, the lysimeter area is surrounded by aluminium plates covered with tin foil in order to avoid a contamination of the surrounding area and to control - for balance purposes - the amount of ^{14}C-labelled pesticide not reaching the lysimeter area. Several treatments have shown that up to 20 % of the applied pesticide does not reach the experimental area (27). This has to be taken into account when planning the application of defined rates of a certain pesticide. This problem does not occur in experiments where seeds are sown that have been treated with a ^{14}C-labelled pesticide (31-35).

The Lysimeter Concept.

The results of extensive experiments with a total of about 50 ^{14}C-labelled organic chemicals combining laboratory, microecosystem, pot and lysimeter experiments have led to the concept of studying the long-term behaviour of organic chemicals in agroecosystems (Table I). In particular, more than 20 Ph.D. theses specially designed to fill gaps in knowledge have contributed considerably to this concept. All the experiments are grouped around practice-related lysimeter experiments using ^{14}C-labelled compounds (Figure 2, Table II). The labelling position depends on the questions under investigation. The results yield information about uptake and metabolism in treated

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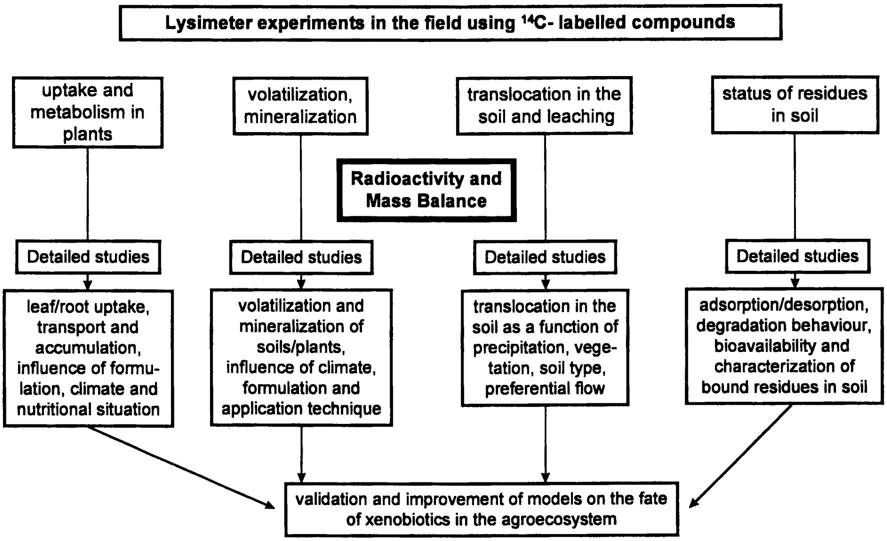
Table I. The Concept of Studying the Long-Term Behaviour of Organic Chemicals in the Agroecosystem.


Lysimeter experiments in the field using ¹⁴C- labelled compounds
uptake and metabolism in plants
volatilization, mineralization
translocation in the soil and leaching
status of residues in soil
Radioactivity and Mass Balance
Detailed studies
Detailed studies
Detailed studies
Detailed studies
leaf/root uptake, transport and accumulation, influence of formulation, climate and nutritional situation
volatilization and mineralization of soils/plants, influence of climate, formulation and application technique
translocation in the soil as a function of precipitation, vegetation, soil type, preferential flow
adsorption/desorption, degradation behaviour, bioavailability and characterization of bound residues in soil
validation and improvement of models on the fate of xenobiotics in the agroecosystem

plants as well as untreated rotational crops (13, 14), about volatilization and mineralization (16), about translocation and leaching in soil (36) and about the disposition of residues in soil (12). The range of data can be seen in Table II. In order to elucidate the processes involved, detailed experiments are designed, e.g. to study leaf or root uptake, translocation and accumulation in plants and the effects of formulation and of climatic factors like temperature, humidity and irrigation as well as the nutritional status of the plant on uptake and metabolism (Table I). In the following, the five major research topics of special interest for improving the use of pesticides are briefly outlined.

Uptake and Metabolism in Plants. The lysimeter experiment yields precise information on the uptake and internal distribution of the applied compound as well as the metabolites, describing the status of residues, especially in those plant parts relevant for human and animal nutrition. In lysimeter experiments it is not only possible to quantify the residues in the treated plants (37), but also the carry-over to rotational crops, which is of special interest for evaluating complete plant protection measures (13,14).

With high-specific-radioactivity labelling it is also possible to identify those traces of radiocarbon which are assimilated as the product of mineralization, namely labelled $^{14}CO_2$, and thus represent just natural carbon as was demonstrated in a lysimeter experiment with [3-^{14}C]metamitron applied preemergence to sugar beets (38). It was possible to identify 800 mg of metamitron equivalent as ^{14}C in the hectare yield of sucrose which no longer represented a residue in the sense of the definition.

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Table II. Selected Lysimeter Studies with Undisturbed Soil Columns (1.1 m Depth) in the Institute of Radioagronomy from 1983-1994: Radioactivity Balances at the End of the Experiments.

Net applied radioactivity = 100 %

Compound	*Soil type*	*First crop*	*Date of application*	*End of study*	*Radioactivity found in* Soil[a] %	Plants[b] %	Leachate[b] %	*Total* %	*Ref. no.*
Atrazine	OL	maize	May 1989	June 1991	41.1	7.9	2.0	51.0	40
	GC	maize	May 1989	June 1991	33.6	6.4	2.0	42.0	40
Chloridazon	OL	sugar beet	April 1989	May 1991	76.7	2.0	0.3	79.0	41
	GC	sugar beet	April 1989	May 1991	64.4	3.0	7.1	74.5	41
CL 23601	OL	maize	July 1991	July 1991	59.7	0.1	<0.1	59.8	42
	GC	maize	July 1991	July 1991	65.6	0.2	0.2	66.4	42
Clopyralid[c]	OL	sugar beet	June 1988	Aug. 1990	20.4	19.9	0.6	40.9	43
Clopyralid	GC	sugar beet	June 1989	July 1991	13.2	12.2	0.4	25.8	43
Clopyralid[d]	GC	oilseed rape	Feb. 1992	Mar. 1994	9.1	5.8	0.5	15.4	44
Cycloxydym	OL	sugar beet	May 1988	April 1990	14.9	0.5	0.7	16.1	I.R.
Dichloprop-P	OL	summer barley	May 1989	June 1991	19.1	0.2	0.1	19.4	41
	GC	summer barley	May 1989	June 1991	27.3	0.3	0.3	27.9	41
Diflufenican[e]	OL	winter wheat	Dec. 1990	Dec. 1992	55.2	0.2	0.1	55.5	45
Fluroxypyr[c]	GC	summer barley	May 1989	June 1991	41.1	3.7	0.1	44.9	43
Methabenzthiazuron[f]	OL	winter wheat	April 1984	Aug. 1988	42.2	<0.1	0.6	42.8	46
Metamitron[f,g]	OL	sugar beet	May 1983	Aug. 1988	36.3	<0.1	0.6	36.9	46
Pyridate	OL	maize	May 1989	June 1991	46.0	0.5	0.1	46.6	I.R.
	GC	maize	May 1989	June 1991	46.0	1.2	0.3	48.3	I.R.
Quinmerac	OL	summer wheat	May 1988	April 1990	35.2	0.7	0.8	36.7	I.R.
Quinmerac	GC	sugar beet	May 1990	May 1992	31.8	1.0	3.7	36.5	I.R.
Terbuthylazine	OL	maize	May 1989	May 1991	66.5	4.2	3.2	73.9	I.R.
	GC	maize	May 1989	May 1991	64.0	4.2	10.4	78.6	I.R.

[a]In entire soil core at the end of the study, [b]total of all samples during the study, [c]average of 2 lysimeters, single and double application rate, [d]average of 2 replicates, [e]average of 2 lysimeters, one with repeated application in the 2nd year, [f]average of 4 lysimeters (2 single and 2 double application rate), [g]above ground lysimeters of 0.85 m depth, OL = orthic luvisol, GC = gleyic cambisol, I.R. = Internal Report, Institute of Radioagronomy.

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In many respects, this lysimeter approach to studying the fate of pesticides in the agro-ecosystem offers additional information for optimizing pesticide use (2). In general, only a few percent of an applied pesticide reaches and finally enters the plant to perform its intended function. As one example, several lysimeter experiments have been conducted with barley and wheat to study the influence of formulation, early and late sowing, as well as precipitation on the uptake and translocation of seed-dressed [benzene ring-U-^{14}C]triadimenol (31, 32). The total plant uptake amounted to about 5 % of the applied radioactivity and between 70 and 90 % of the ^{14}C was still present as unchanged triadimenol. Depending on the rainfall intensity and distribution after sowing, up to 80 % of the applied radioactivity was washed off the treated seed into the surrounding soil, from where roots could take up a further supply of active ingredient (31, 32).

Macro-, semimicro- and microautoradiography in combination with residue analysis (39) provide detailed information on the penetration of pesticides into germinating seeds, root and leaf surfaces, on barriers as well as routes of entry, on translocation (systemic behaviour) and internal distribution. Especially in insecticide and fungicide research such comprehensive information about absorption by plants and spheres of activity, supplemented by biological testing (e.g. aphids, mildew infestation), is a prerequisite for improving formulation characteristics and the timing of application as demonstrated recently by comprehensive studies on the uptake of the insecticide [pyridinyl-^{14}C-methylene] imidacloprid after seed treatment of wheat (Figure 4), sugar beets (33, 34), cotton (35), and after bark application to apple and citrus trees (Mendel, R., Institute of Radioagronomy, personal communication, 1997). Only detailed studies of this type in connection with outdoor lysimeter experiments will produce the information needed to determine the least active ingredient concentration inside the plant and its bioavailability.

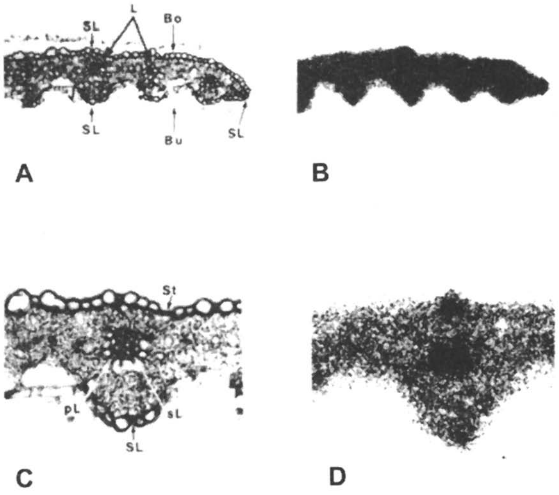

Figure 4. Autoradiographic Localisation of Radiocarbon in the First Wheat Leaf (B and D) Demonstrating Uptake and Xylem Transport of [pyridinyl-^{14}C-methylene]Imidacloprid after Seed Treatment. A and C Enlargements of Kryocuts.

Volatilization and Mineralization. Volatilization from treated areas is a major source of pesticide residues in air, fog and rain, and thus may lead to a long-range transport of pesticide residues to areas remote from their application (47). In contrast, mineralization of pesticides, resulting in the emission of CO_2 as the final degradation product, acts as a natural detoxification process in agroecosystems. There are some important aspects to be noted concerning the measurement of these gaseous losses:

- In lysimeter studies it was not possible to obtain data concerning gaseous losses, so that radioactivity and mass balances were usually incomplete (Table II).
- Micrometeorological measurements of pesticide volatilization in the field are laborious and expensive. Due to field inhomogeneities, (micro)meteorological assumptions and the measurement of low pesticide concentrations in air, field measurements of pesticide volatilization are subject to a relatively high variance.
- Consequently, up to now most of the information has been derived from laboratory experiments under artificial laboratory conditions.

In order to close the balance gap in lysimeter experiments, a glass wind tunnel (Figure 5) has been set up above a 0.5-m^2 lysimeter (30, 48), allowing the measurement of volatile losses of ^{14}C-labelled chemicals after application by methods comparable to agricultural practice. Passing a control plot as a windbreak, clean air is forced over the lysimeter by a blower/air conditioning unit and is subsequently released into the atmosphere after air mixing and sampling. At the beginning of a volatilization experiment, radioactive spray mixtures are applied by a semiautomatic sprayer (16, 48), which guarantees a practice-like application (droplet spectrum, application volume etc.) in combination with a highly homogeneous distribution onto the target surface.

Since experiments should be conducted as close as possible to field situations (semi-field conditions), the climatic scenario inside the wind tunnel (air temperature and wind speed, range: 0.3-3.5 m s^{-1}) is permanently adapted to outside conditions. Even a climatic scenario of a reference field can be transferred online into the wind tunnel via dedicated line and modems. The air flow profile inside the wind tunnel is adapted to the boundary layer flow profiles above bare soil or inside/above plants. Precipitation can be simulated with nozzles mounted in the lid of the wind tunnel. The whole wind tunnel is made of UV-transparent materials (side walls: borosilicate glass,

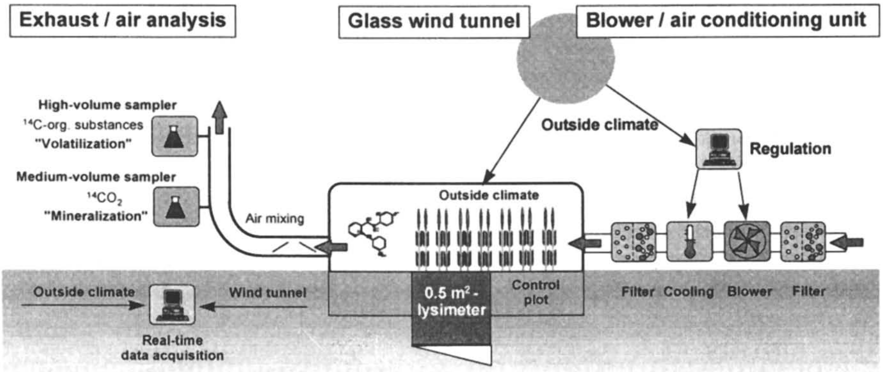
Exhaust / air analysis
Glass wind tunnel
Blower / air conditioning unit
High-volume sampler
^{14}C-org. substances
"Volatilization"
Medium-volume sampler
$^{14}CO_2$
"Mineralization"
Outside climate
Regulation
Air mixing
Outside climate
Outside climate
Wind tunnel
0.5 m² - lysimeter
Control plot
Filter
Cooling
Blower
Filter
Real-time data acquisition

Figure 5. Diagram of the Wind Tunnel at the Institute of Chemistry and Dynamics of the Geosphere 5: Radioagronomy.

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lid: acrylic glass), allowing direct photolysis on leaf or soil surfaces. Although irradiation is reduced by shading, soiling, etc., surface temperatures correspond well to the field situation.

Representative aliquots of the outlet air are taken continuously with two separate air samplers after intensive mixing by special air mixers (49). Due to relatively large sample volumes, low detection limits are achieved (16, 48). ^{14}C-labelled organic substances that volatilize are sampled isokinetically with a high-volume sampler. The sampling head, consisting of a binder-free glass-fibre filter (185 mm Ø) and an adsorption bed of precleaned polyurethane foam (PUF, 100 mm o.d., 3 x 50 mm), is directly attached onto the exhaust. The maximum sampling rate is 50 $m^3 h^{-1}$. For each compound the quantitative sampling of its vapours is tested prior to a wind tunnel experiment. The sampling head is regularly replaced (1-24 h). Filters are Soxhlet-extracted and the PUF plugs are extracted using a special squeezing apparatus (16, 48, 50). $^{14}CO_2$ resulting from total degradation of the test compound is sampled with a medium-volume sampler (51). The maximum sampling rate is 3.5 L min^{-1}. After adsorption of ^{14}C-labelled organics and intensive drying of the air sample, $^{14}CO_2$ is quantitatively absorbed in 2-methoxy-propylamine (Carbosorb E^+) using a specially cooled intensive wash bottle. The maximum integration period is 48 h, corresponding to 10 m^3 of air.

At the end of the experiments contaminated soil layers and plants are completely removed. Leachate is pumped off, and the wind tunnel is decontaminated using solvents. Radioactivity in air, soil, plant and leachate samples is measured by liquid scintillation counting, characterization of the unchanged ^{14}C-labelled test compound or its metabolites is done by radio-TLC and radio-HPLC.

With the addition of this wind tunnel to the lysimeter setup, a complete radioactivity and mass balance and thus a comprehensive picture concerning the fate of pesticides and other organic chemicals in all compartments of the agroecosystem can now be obtained in a semi-field experimental design. This has been documented in several experiments investigating the volatilization of pesticides and PAH (16, 52, 53). Typical ^{14}C recoveries ranged from 97 to 103 %.

Each wind-tunnel experiment takes place under individual, non-repeatable semi-field conditions just as field and lysimeter experiments do. Thus the wind tunnel combines the advantages of laboratory facilities (use of radioisotopes, air analysis) and field studies (semi-field conditions) and represents a link between laboratory experiments and genuine field tests. Recently it has been shown that results obtained with the windtunnel correspond well to field measurements, especially for volatilization from plant surfaces. Additional information will be compiled by Stork et al. in Chapter 3 of this volume of the Symposium Series.

Distribution, Translocation and Leaching in Soil. The translocation and movement of residues into ground-water basins have received considerable attention especially in the European Community (5, 10, 54). Lysimeter studies in combination with detailed experiments contribute considerably to clarifying the occurrence of translocation and preferential flow as a function of soil parameters, precipitation and practical measures like the application of organic amendments.

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In 1983 extensive experiments were carried out with the herbicide [carbonyl-^{14}C]methabenzthiazuron formulated as TRIBUNIL® and sprayed postemergence onto winter wheat in concentrations relevant to agricultural practice (37, 46, 55). At the time of wheat harvest, 127 - 133 days after spraying MBT, about 36 % of the applied radioactivity was still identified in the soil as the active ingredient and its metabolites. These residues were almost entirely retained in the upper 5 cm of the plough layer, and very little was translocated into the 5-10 cm layer. These results already indicate that in the soil great differences in concentrations are found between the top millimetres as the first input compartment of spray-applied pesticides and the underlying soil layers. Further distribution is then effected to a greater extent by mechanical working of the soil than by translocation processes as a consequence of precipitation events and the movement of water.

In these lysimeter experiments, the drainage runoff of a field situation is roughly simulated by the leachate discharge. Over a period of 3-4 years, 20-30 % of the annual precipitation (600 mm) was collected, primarily during the winter months and as individual events after heavy rainfall at the beginning of the growing season (rotation: winter wheat, winter barley, sugar beets). A total of 0.5 % of the applied carbonyl-^{14}C was found in the total leachate (46). In additional lysimeter experiments [phenyl-U-^{14}C]methabenzthiazuron was sprayed preemergence onto winter wheat. The leaching results in connection with data from soil solutions, withdrawn via suction candles from the plough layer and the Bt_1 horizon (40 cm) of the orthic luvisol, gave special information on the transport situation and the dissolved organic carbon in general (25, 56). The amendment of maize straw (equivalent to 9 t ha^{-1}) simulating the rotational situation of maize followed by winter wheat considerably enhanced the degradation of methabenzthiazuron to the major metabolite demethyl-methabenzthiazuron and the formation of bound residues in soil. This effect reduced the average load of methabenzthiazuron in the leachates to just 0.02 μg L^{-1} as compared to 0.04 μg L^{-1} for a lysimeter without organic amendment (56), demonstrating that retention and degradation processes eliminate the amount available for transport. In detailed experiments using undisturbed soil columns of up to 20 cm in diameter, the role of dissolved organic carbon in the soil solution as the transport medium for pesticide residues in soils is now being investigated. ^{14}C-labelled, as well as ^{13}C-depleted, plant material is introduced to stimulate soil organic matter turnover and to explore new ways to study the binding of residues using ^{13}C-labelled pesticides (57, 58).

The transport of pesticides from the plough layer into the unsaturated root zone or even into the ground water is governed by many factors. Only the measurement of important crucial variables like soil moisture content and time and intensity of precipitation offers the chance for further interpretation (59). Especially in structured soils the preferential flow apparently plays an important role as far as the translocation of pesticide residues is concerned. In a number of lysimeter experiments using orthic luvisol, the concentration in leachates, especially after dry periods, reflected concentrations found in the soil solution of the plough layer (25, 46, 60). Again, in combination with lysimeter experiments the application of brilliant blue, bromide or deuterium-labelled water provides insight into leaching processes (61). Channels open to macropore flow,

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a special kind of preferential flow, become visible with the help of computer tomography (62, 63). X-ray microtomography as a high-resolution non-destructive imaging technique has been established at the Research Centre Jülich for application in soil science. Continuous soil pores with diameters down to 50 µm can be identified in soil cores with a diameter of up to 8 cm (63). In combination with conventional measurements of hydraulic properties this information will hopefully lead to further insights into flow phenomena in soil.

Several chapters presented in this volume by Bergström and Shirmohammadi, Flury et al., Jene et al., and Pütz et al. will give additional comprehensive information on transport processes in soil.

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Status of Residues in Soil. The soil itself is a bioreactor. For example, an orthic luvisol under the cultivation and climatic conditions of the Federal Republic of Germany releases about 3.5 - 5.0 t ha^{-1} of carbon per year to the natural carbon cycle in the form of CO_2 (12). Pesticides and their metabolites are in general also subject to these intensive conversion processes and are finally mineralized. Lysimeter and detailed laboratory experiments have indicated that even relatively small amounts of maize straw, equivalent to just 1.5 t ha^{-1}, stimulate soil microbial activity and hence considerably affect the degradation of methabenzthiazuron in soil (56).

The soil organic matter consists of a large number of ring structures, bridges and functional groups which may bond covalently with pesticides and metabolites. The complex structure of natural humic substances, as well as the extremely wide concentration ratio between pesticides and organic reaction sites in soil, make it difficult to study their interaction products. As a complement to lysimeter studies, laboratory experiments under defined conditions are therefore necessary to investigate in particular degradation, binding and release of pesticides in topsoil and subsoil. ^{13}C-NMR spectroscopy in conjunction with gel-permeation chromatography enables the observation of the chemical surroundings of carbon atoms and their relation to the respective pesticide fixed in soil organic matter fractions (57, 58). In this volume Burauel et al. present the state of the art as summarized during a workshop organized on behalf of the German Research Foundation (DFG) and held at Jülich, Germany, in September 1996.

The Bioavailability of Residues. With the data set of a lysimeter experiment as described here, a complete picture can be obtained concerning the long-term behaviour of a pesticide (Figure 6). The data plotted over time give information on the losses by volatilization/mineralization, uptake by plants and leaching as well as on the residues in the soil (adsorbed - fixed - bound) and in particular on that portion which may still be bioavailable. This information is of special interest for the assessment of plant protection products as far as their possible effects on non-target organisms are concerned (4). This involves recognizing and determining the concentration of pesticide residues in soils or plants and their spatial distribution, but also the biologically available portion at the time of the observed effect at the location of the event (13). Over the long range of the growing season, the plant integrates the uptake situation over time as a function of the physicochemical behaviour of the respective pesticide, reflecting turnover and biological availability as a function of soil and climatic factors. This detailed

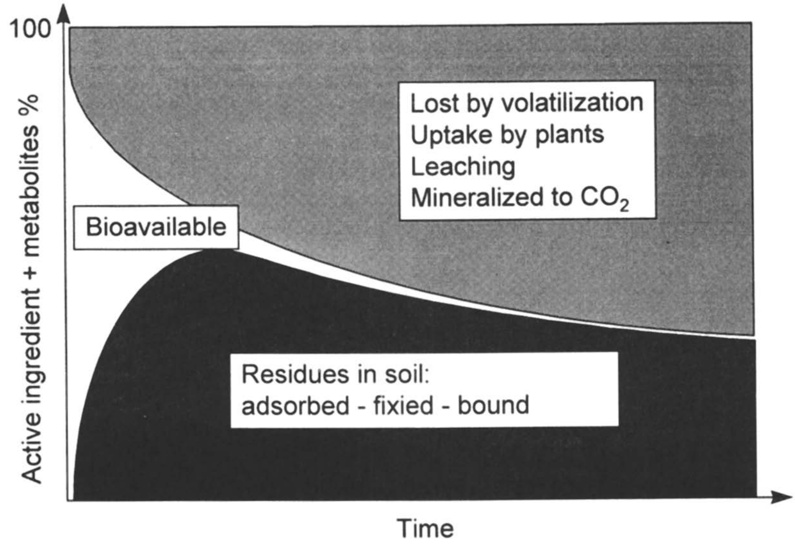

Figure 6. The General Fate of Organic Chemicals in Soil.

information is an essential prerequisite for assessing the exposure of, e.g. soil organisms, in order to link an observed effect to the occurrence of a potentially active ingredient. However, the most important question which remains to be clarified is the extent to which analytically determined residue values in soils are ultimately bioavailable for certain organisms and so the chemical residues are thus able to exert an influence on the organisms or the organisms are able to transform the chemical. The lysimeter experiment, in combination with detailed studies and specially designed small-scale experiments (Table I), could be used as an approach to gain additional information on the dynamics of the situation of the bioavailability of residues throughout a growing season. This approach should then be combined with field studies on side effects for non-target organisms (4).

Scaling up and Modelling.

The use of mathematical models to assess the environmental fate of pesticides is increasing (64). The broader use of such models, for example in a regulatory setting, implies that these models have been tested extensively. High-quality data sets are to be used for this procedure (65). With the aid of sophisticated data sets originating from lysimeter experiments, the validation and improvement of simulation models on the long-term behaviour of xenobiotics in agroecosystems can thus be achieved.

To better understand the relevant processes concerning the persistence and especially the translocation of pesticides on different scales, the FELS study (= Field - LysimEter - Laboratory - Simulation) was conceived. Differences in relevant processes affecting the fate of pesticides in a lysimeter compared to the laboratory/field situation will be investigated and used for modelling. Pütz et al. present this project

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more in detail in this volume. Within this study the effect of the variability of crucial properties on the field scale relevant to the environmental behaviour of pesticides will be analysed:

- Transferability of results from lysimeter experiments to the field situation.
- Identification of characteristic processes which essentially influence the behaviour of pesticides in the agroecosystem and/or in the lysimeter, as well as the description of process parameters in the laboratory system, lysimeter and field.
- Use of the measured data to validate and further develop simulation models. The contributions by Kubiak, Pütz et al. and Vereecken and Dust enlarge on this topic.
- Improvement of the interpretation of field ecotoxicological studies.

Conclusions

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Lysimeter experiments in combination with detailed studies as outlined in Table I yield results which lead to practical recommendations for the improvement of pesticide use, not only to ensure proper application and optimal uptake, especially in the case of fungicides and insecticides, but also to influence their further fate in the final sink, the soil. Data compiled in lysimeter studies and utilized to make practical recommendations will be of special interest in integrated pest management. One major conclusion of several lysimeter workshops is that all measures which improve soil fertility reduce possible side effects of pesticide residues in agroecosystems, too.

Lysimeters similar to those described here have been successfully developed and used in recent years by a number of industrial laboratories (66, 67) and specialized research teams including the Fraunhofer Institute of Environmental Chemistry and Ecotoxicology (68), Schmallenberg, Germany, the Institute of Soil Ecology, GSF-Research Centre of Environment and Health (69), Munich, Germany, the Landeslehr- and -forschungsanstalt (70), Neustadt, Germany, NATEC (71), Hamburg, Germany and others. Close cooperation with scientists from the Nuclear Institute of Agriculture and Biology, Faisalabad (Pakistan) and the Chung Buk University (72, 73), Cheong Ju (Korea), and CENA, Piracicaba (Brazil) has led to similar setups in their research establishments. It is of vital interest to improve the use of pesticides, especially in these countries. The IAEA Vienna initiates and supports cooperation in this field of research which ensures immediate transfer of knowledge to the users in developing countries as part of the responsibility of the industrial countries as pesticide producers. Plimmer et al. enlarge on these thoughts in the last chapter of this volume.

In lysimeter studies conducted in accordance with good laboratory practice (GLP), the data required for exposure assessment are generated, and exposure scenarios are characterized. Therefore, the lysimeter concept is now clearly a valuable and comprehensive contribution to pesticide research. Since 1990 the lysimeter experiment has been an integral part of registration requirements in Germany for pesticides which show leaching tendencies (29). However, this guideline reduces the value of the lysimeter experiment to just an aged leaching test under realistic outdoor conditions. Since all companies still engaged in developing pesticides now have lysimeter facilities available, there will be no new compound introduced into the market which has not already been tested in lysimeter experiments at an early stage of development due to all the advantages demonstrated and discussed above. As outlined in Table I, in combination with data from standardized laboratory and field tests, a more profound evaluation of the risks and benefits of a compound is possible (3). Therefore, legislation will increasingly specify this data combination for assessment procedures as already demonstrated in the confidential dossiers of the German authorities as a basis for evaluating environmental risks during final discussions with the government pesticide committee as outlined in the contributions by Nolting and Schinkel as well as Klein and Kördel in this volume.

Acknowledgments. The pesticide data presented are part of a long-term cooperation between the Agricultural Centre Monheim, Bayer AG Leverkusen, and the Institute of Radioagronomy, Forschungszentrum Jülich. Additional support came from German Research Foundation (DFG), Bonn, and German Federal Environmental Foundation, Osnabrück, Germany.

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Chapter 2

Volatilization of Pesticides: Measurements Under Simulated Field Conditions

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Volatilization of pesticides is either measured under artificial, constant conditions in the laboratory or using micrometeorological measurements in the field, both having their specific limitations. A wind tunnel erected above a lysimeter combines the advantages of both methods: simulated field conditions, use of radiolabeled compounds, detection of metabolites and mass balances.
The volatilization behavior of four pesticides was studied under simulated field conditions in the wind tunnel. In two experiments, simultaneous, parallel measurements were carried out in the field. High volatilization rates from plants were detected for fenpropimorph and parathion-methyl (up to 50 % d^{-1}) whereas clopyralid showed only a very low volatilization. Generally, volatilization started immediately after application at relatively high rates, rapidly decreasing to a considerably lower level, where a diurnal rhythm was observed. Volatilization rates corresponded well with data from the simultaneous field measurements. Plant uptake was a major process counteracting pesticide volatilization. Volatilization from bare soil was only slight for parathion-methyl (2 %) and terbuthylazine (0.5 %) during a 3-week wind-tunnel experiment. The volatilization rates were strongly dependent on soil moisture. A diurnal rhythm was observed right from the beginning. Simultaneously measured volatilization rates in the field were considerably higher due to differences in soil moisture, application volume of water, and irrigation intensity. The occurrence of non-identified metabolites in air samples suggests that for many pesticides metabolic processes, possibly due to photolysis on plant or soil surfaces plays an important role in their dissipation.

In The Lysimeter Concept; Führ, F., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 1998.

For many pesticides, volatilization is a major process contributing to fate and behavior in the environment. Besides spray drift, wind erosion and industrial production, volatilization is probably the most important source of pesticide residues in air, fog, and rain *(1-3)*. Photolytically stable compounds may be transported over long distances in the atmosphere, which can finally contribute to a contamination of remote ecosystems with pesticides or their degradation products via dry or wet deposition *(4)*.

Pesticide volatilization is a very complex process, being dependent on the physico-chemial properties of a compound (e.g. Henry's law constant, vapor pressure, water solubility, partition and adsorption coefficients, photolability), environmental factors (e.g. bare soil versus leaf surfaces, surface temperature, soil moisture, precipitation, evaporation) and type of formulation and other application practices (e.g. soil surface application vs. soil incorporation, droplet spectrum, spray volume). Adsorption and its dependence on soil moisture is the most important factor reducing volatilization from soil *(3,5,6)*. Due to adsorption, volatilization from soils is generally much lower compared to volatilization from plants *(7-9)*. Although the sorption capacity of plant surfaces is considered to be much lower compared to soil, it has to be emphasized that plant surfaces are interfering surfaces since absorption into and uptake through the cuticle are processes antagonistic to pesticide volatilization. In the natural environment, besides volatilization, direct and indirect photolysis may additionally reduce the amount of pesticides present on the surface. Due to the complexity and interaction of volatilization with other processes, realistic data can only be obtained from experiments which simulate the most important parameters.

In the past, the volatilization of pesticides was either measured under artificial, constant conditions in the laboratory using small volatilization chambers *(10-12)*, microagroecosystems *(13-15)*, wind tunnels *(16-18)* or in the field, using various micrometeorological methods *(19-21)*. Sometimes small volatilization chambers were also used in the field or on lysimeters *(22-24)*, but the climate inside these chambers differs considerably from outside conditions due to the greenhouse effect. Dissipation experiments (indirect method), which just measure pesticide residues on the target surfaces, cannot differentiate between losses due to volatilization and sorption followed by the formation of metabolites and non-extractable residues. The main advantages of laboratory experiments are their reproducibility and the use of radiolabeled compounds. This allows the detection of metabolites including $^{14}CO_2$ as the final degradation product (= mineralization) and the establishment of mass balances. Results of laboratory experiments are limited by extrapolating to a real field scenario. Micrometeorological measurements in the field are very laborious and costly and, like any field experiment, the error margin is comparatively high. Because the use of radiolabeled compounds is prohibited in the field, a complete detection of metabolites or non-extractable residues is impossible for most of the compounds.

The aim of the investigations presented here was to (a) obtain data regarding pesticide volatilization under the most realistic conditions, directly transferable to a real field scenario, (b) obtain complete radioactivity balances in lysimeter experiments, which has not been possible so far (see Table II in Chapter I) and (c) compare results of wind-tunnel experiments with simultaneous micrometeorological measurements in the field.

Experimental Methods

Wind Tunnel. A glass wind tunnel was erected above a 0.5-m^2 lysimeter *(18,25,26)*. The climate inside the wind tunnel is continuously adapted to outside conditions or to the scenario of a reference field *(27)*. Thus each wind-tunnel experiment took place under unique, non-repeatable conditions, like in field or lysimeter experiments in general. All experiments with or without vegetation were conducted using ^{14}C-labeled compounds. Air samplers allowed sensitive and continuous measurements of gaseous emissions from volatilization (^{14}C-labeled organic compounds) and mineralization ($^{14}CO_2$). The wind tunnel combines the advantages of laboratory and field experiments: semi-field conditions, use of radiolabeled compounds, detection of metabolites and complete material balances. A brief description of the wind tunnel and corresponding air analysis is given by Führ et al. in Chapter I of this volume.

Two experiments (DLO-1 and DLO-2, Table II) were accompanied by field experiments using non-radiolabeled compounds. The spraying of the pesticide mixtures was performed at the same time with balanced application rates. To obtain the same experimental conditions, the field climate (wind speed 20 cm above surface and air temperature) was transferred online to the wind tunnel via modems. Air sampling in the wind tunnel was conducted continuously during the experiments (see Chapter I) and at intervals simultaneously with sampling in the field. In the field, air sampling was performed at three heights above the surface (0.2, 0.5 and 0.8 m) with 13 (DLO-1) and 10 (DLO-2) sampling intervals, each of 1-2 h duration, downwind the treated field. The sampling flow was 50 L min^{-1} and the pesticides were adsorbed on batches of 10 g XAD-4 (0.3-1.0 mm grain) held in glass tubes (35 mm i.d.). The aerodynamic method and the Bowen ratio method were applied to calculate the pesticide flux into the atmosphere *(20,28)*. Meteorological data were recorded in the field as required by micrometeorological methods. Details are given in *27* and *29*.

Compounds. Four pesticides, covering a broad range of physico-chemical properties (Table I), were chosen as model compounds. Clopyralid is a selective systemic herbicide for the post-emergence control of broad-leaved weeds. There is no information available about its volatilization behavior, but lysimeter balances were highly incomplete (Table II in Chapter I). A low volatilization tendency is indicated by the low Henry's law constant of $7.7 \cdot 10^{-9}$ (Table I), mainly caused by a very high water solubility. Fenpropimorph is a systemic fungicide with protective and curative action. Parathion-methyl is a non-systemic insecticide and acaricide with contact, stomach, and some respiratory action. Both, parathion-methyl and fenpropimorph, are known to be very volatile after application onto plants but hardly volatile after application onto bare soil *(7,18,30-33)*. Terbuthylazine, the replacement product for atrazine, which was banned in Germany in 1992 *(34)*, is a broad-spectrum pre- or post-emergence herbicide. Its volatility was reported to be low after soil application *(23)*.

In the wind-tunnel experiments, formulated [2,6-^{14}C]clopyralid (^{14}C-CLO, Dow AgroSciences, Indianapolis, USA, 98 % radiochemical purity (RP)), [phenyl-U-^{14}C]fenpropimorph (^{14}C-FEN, BASF AG, Germany, 85 % RP), [phenyl-U-^{14}C]parathion-methyl (^{14}C-PM, BAYER AG, Germany, 99 % RP) and [2,4,6-^{14}C]terbuthylazine (^{14}C-TER, Novartis, Switzerland, 97 % RP) were used.

Table I. Physico-Chemical Properties of the Investigated Compounds *(35)*.

Common name	*Clopyralid*	*Fenpropimorph*	*Parathion-methyl*	*Terbuthylazine*
	Herbicide	*Fungicide*	*Insecticide*	*Herbicide*
Chemical family:	Pyridine derivative	Morpholine derivative	Organo-phosphorus	Triazine
Molec. formula:	$C_6H_3O_2Cl_2N$	$C_{20}H_{33}NO$	$C_8H_{10}NO_5PS$	$C_9H_{16}ClN_5$
Molec. weight:	192.0	303.5	263.2	229.7
Heat of vaporiz.:	100.0 kJ mol^{-1}[a]	98.4 kJ mol^{-1}[b]	109.3 kJ mol^{-1}[c]	92.6 kJ mol^{-1}[b]
Vapor pressure[d]:	$7.7 \cdot 10^{-6}$ hPa	$2.3 \cdot 10^{-5}$ hPa	$1.1 \cdot 10^{-5}$ hPa[c]	$1.5 \cdot 10^{-6}$ hPa
Water solubility:	7850 mg L^{-1}	4.3 mg L^{-1} (pH 7.2)	55 mg L^{-1}	8.5 mg L^{-1}
K_H: [e]	$7.7 \cdot 10^{-9}$[f]	$6.7 \cdot 10^{-5}$	$2.2 \cdot 10^{-6}$	$1.7 \cdot 10^{-6}$
K_{ow} log P:	2.33 10^{-3} (pH 7)	4.1 (pH 7.2)	3.0	3.0
K_{oc}:	4[g]	862-4500	230-670[h]	162-278

[a]estimated, [b]Stamm, Novartis, personal communication, [c]from *(33)*, [d]standardized to 20°C according to Clausius-Clapeyron *(36)*, [e]dimensionless Henry's law constant @ 20° C, [f]calculated from water solubility and vapor pressure, [g]from *(37)*, [h]from *(38)*.

Experiments. The test compounds were investigated under individual scenarios. The eight wind-tunnel experiments and experimental conditions are compiled in Table II. For net applied amounts no correction for RP was performed, except experiments FEN-EC1+2 because of a low RP of ^{14}C-fenpropimorph. Experimental periods varied from 90 h (FEN-EC1) to 186 h (DLO-1). Most of the plant experiments were conducted with dwarf beans, which is the standard plant for pesticide volatilization experiments in Germany according to BBA guideline IV, 6-1 *(39)*, using a semiautomatic sprayer *(18,25)*. Two different formulations of parathion-methyl (WP and EC) were used. For the replicate experiments FEN-EC2 and PM-EC2 the activated carbon filter in the air inlet was removed (Table II), allowing more indirect photolysis on the leaf surfaces due to more ambient atmospheric radicals or precursors entering the wind tunnel. Clopyralid was applied onto oil-seed rape and sugar beet according to its agricultural use.

At the end of the experiments, the lysimeter plants were completely harvested and subsequently rinsed with water, methanol and chloroform. Contaminated soil layers were completely removed and the wind tunnel was decontaminated with solvents. All samples (air, plant, soil, leachate) were measured for radioactivity by liquid scintillation counting. Compound characterization was performed by radio-TLC and radio-HPLC.

Two of the eight wind-tunnel experiments (DLO-1 and DLO-2) were conducted in parallel with simultaneous field experiments (Table III). In experiment DLO-1, fenpropimorph, parathion-methyl and terbuthylazine were applied in a tank mixture onto bare soil in May 1995. ^{14}C-labeled parathion-methyl and terbuthylazine were in the wind-tunnel experiment. A mixture of clopyralid and fenpropimorph was applied onto sugar beet in June 1996 (DLO-2). In this case, the application time (BBCH 39) was chosen especially to achieve an optimal comparison of a bare soil versus a foliar application. Only clopyralid was ^{14}C-labeled in the wind-tunnel experiment.

Table II. Data of Selected Wind Tunnel Experiments in 1993-1996.

	Fenpropimorph		*Parathion-methyl*				*Clopyralid*	
Abbrev.	*FEN-EC1*	*FEN-EC2*	*PM-WP*	*PM-EC1*	*PM-EC2*	*DLO-1*	*CLO-1*	*DLO-2*
Formulation:	EC[a] "Corbel"		WP[b] "ME 605"	EC[a] "Methyl-bladan"		WP[b] "ME 605"	WSC[c] „Lontrel"	
Start:	28. July 1994	22. June 1995	13. July 1993	19. Sept. 1994	12. July 1995	11. May 1995	28. Mar. 1996	25. June 1996
End:	01. Aug. 1994	30. June 1995	19. July 1993	26. Sept. 1994	19. July 1995	31. May 1995	02. April 1996	01. July 1996
Duration:	90 h	186 h	144 h	162 h	162 h	474 h	114 h	143 h
Net applied:	572 g a.i. ha^{-1}	427 g a.i. ha^{-1}	68 g a.i. ha^{-1}	172 g a.i. ha^{-1}	163 g a.i. ha^{-1}	**Pesticide mixture, see Table III**	118 g a.i. ha^{-1}	**Pesticide mixture, see Table III**
Crop:	Dwarf beans (first blossom)					Bare soil	Rape	Sugar beet
Plant age:	7.5 weeks	8.0 weeks	7.0 weeks	7.0 weeks	7.0 weeks	-	32 weeks	8 weeks
Soil coverage.:	≈ 100 %					0 %	≈ 60 %	≈ 100 %
Climatic parameters (averages)								
Air temp.:	26.8° C	21.3° C	19.4° C	15.4° C	22.3° C	12.8 °C	1.7° C	15.0° C
Ø 24 h[d]	24.3° C	15.0° C	18.8° C	12.3° C	23.5° C	11.9 °C	3.9 °C	13.4 °C
Irrig. (sum):	0 mm	15 mm	0 mm	0 mm	15 mm	31 mm	4 mm	10 mm
Wind velocity[e]:	1.0 m s^{-1}	1.0 m s^{-1}	0.9 m s^{-1}	1.2 m s^{-1}	1.0 m s^{-1}	1.1 m s^{-1}	1.6 m s^{-11}	1.0 m s^{-1}
AC[f] filter:	yes	no	yes	yes	no	no	no	no

[a]Emulsion concentrate, [b]wettable powder, [c]water soluble concentrate, [d]average within 24 h after application, [e]20 cm above target surface, [f]activated carbon filter in air inlet.

Table III. The Simultaneous Application of Pesticide Mixtures in the Field and in the Wind Tunnel.

Experiment	*DLO-1 (1995)*		*DLO-2 (1996)*	
	Field	***Wind tunnel***	***Field***	***Wind tunnel***
Vegetation:	none (bare soil)		sugar beet	
Start:	11 May, 14:32	11 May, 14:32	25 June, 15:14	25 June, 15:14
End:	26 May, 14:00	31 May, 8:00	01 July, 14:10	01 July, 14:10
Equipment:	Field sprayer	Special constr.	Field sprayer	Special constr.
Nozzles:	Lurmark Servo Drop 05-110	TeeJet 8004 E	TeeJet XR11003	TeeJet 8004 E
Water [L ha^{-1}]:	202	450 + 450 [a]	212	200 + 117 [a]
Application rates [g a.i. ha^{-1}]				
Clopyralid[b]:	-	-	92	103 (^{14}C)
Fenpropimorph[c]:	1440	1800	691	649
Parathion-methyl[d]:	604	540 (^{14}C)	-	-
Terbuthylazine[e]:	1180	1570 (^{14}C)	-	-

[a] Application volumes of water (+ flushing of spray equipment), [b] water-soluble concentrate, 100 g a.e. L^{-1} (Lontrel), [c] emulsified concentrate, 75 % a.i. (Corbel), [d] wettable powder, 40 % a.i. (ME 605), [e] experimental formulation of Novartis, 50 % a.i., ^{14}C = ^{14}C-labeled.

SOURCE: Adapted from ref. *27*.

Results and Discussion.

Note on the use of ^{14}C-labelled compounds: The expression "radioactivity" represents the unchanged active ingredient ***plus all metabolites and transformation products*** and has to be distinguished from chromatographically characterized active ingredients (a.i.) or metabolites (% AR: applied radioactivity = 100 %, % a.i.: applied active ingredient = 100 %). Comparison with studies using non-radiolabeled compounds can only be made on the basis of characterized compounds.

Radioactivity Balances. Table IV shows the radioactivity balances of the experiments. On average, 98.2±1.0 % AR was recovered in all compartments (air, plant, soil, leachate) plus wall contaminations. Due to high air exchange rates and the use of glass as the major construction material, wall contamination was low in all experiments (< 0.1-0.7 % AR). As a result of the comparatively short experimental periods (90-474 h), soil radioactivity was always concentrated in the uppermost soil layer (0-2(-5) cm). No radioactivity was detected in deeper soil layers (> 20 cm) or in the leachate.

No clear explanation can be given for the increased ^{14}C-residues in soil (22-26 % AR) in experiments FEN-EC1+2. Fenpropimorph is a systemic compound, but no increased ^{14}C-level was measured in the root fraction. This is different from clopyralid, also a systemic compound, where a large amount (23 % AR) was measured in the beet root just 143 h after application. Adsorption of vapors by the surface soil layer is considered, since fenpropimorph has the highest K_{oc} of the investigated compounds (Table I).

Table IV. Radioactivity Balance of Wind Tunnel Experiments in 1993-1996.

All values in % of applied radioactivity.

Experiment	*FEN-EC1*	*FEN-EC2*	*PM-WP*	*PM-EC1*	*PM-EC2*	*DLO-1*	*CLO-1*	*DLO-2*
Contamination	0.7	0.6	0.1	0.1	0.7	0.2	0.2	<0.1
Soil (0-30 cm)	21.8	25.8	2.3	5.2	9.7	93.3	44.1	11.5
Leachate	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Roots	1.4	1.5	n.s.	0.3	1.5	-	n.s.	23.4[a]
Leaves	18.2	26.5	21.9	27.8	26.1	-	53.4	59.8
Volatilization	54.7	37.3	73.3	61.0	60.3	1.8	0.5	1.9
Mineralization	1.0	5.0	0.8	5.1	1.4	2.3	0.1	0.9
Total	97.8	96.7	98.4	99.5	99.7	97.6	98.3	97.5

[a] beet root only, n.s. = roots not separated from soil.

Mineralization ranged from 0.1 to 5.1 % AR in total. For plant experiments, the major part of applied ^{14}C reached the plants. However, slight soil contamination at application cannot be excluded. Additional amounts of ^{14}C could have reached the soil by vapor adsorption and wash-off due to irrigation (Table II), all together leading to considerable amounts of ^{14}C in soil at the end of the experiments (Table IV). Evolved $^{14}CO_2$ is interpreted as (bio-)mineralization of ^{14}C residues in soil, although photomineralization on plant or soil surfaces cannot be excluded.

Volatilization of Fenpropimorph and Parathion-methyl from Dwarf Beans. In total, 37-73 % AR volatilized by the end of the experiments, corresponding to 34-61 % a.i. (Figure 1). Except for FEN-EC2, about 50 % AR (about 40-50 % a.i.) already volatilized within the first 24 h, irrespective of the compound and formulation and the climatic conditions. The initial rapid volatilization (0-24 h) revealed a sharp decrease (Figures 1 and 2), indicating that other processes like foliar uptake counteract the volatilization process. In the further course of the experiments, a long-term release of protected or adsorbed residues occurred on a much lower level. This kinetic of pesticide volatilization from plants has been described previously *(5,18,40)*. In the experiments with 12-h air sampling intervals (FEN-EC1+2 and PM-EC1+2) a diurnal rhythm of volatilization was observed, possibly due to diurnal differences in irradiation and/or temperature at this stage (Figure 2). The cumulative volatilization (Figure 1) fitted well ($chi^2 \leq 0.4$) using associated exponential functions (Equation 1), which allows interpo-

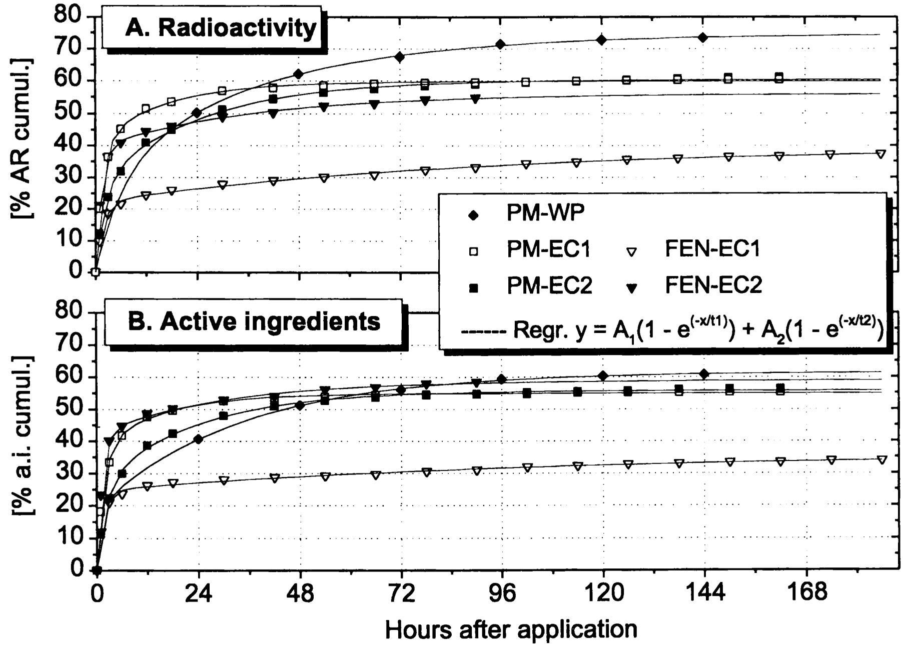

Figure 1. Cumulative volatilization of parathion-methyl and fenpropimorph after application onto dwarf beans.

lation of values (e.g. 24-h values).

$$Y = A_1 \cdot \left(1 - e^{\left(\frac{-x}{t1}\right)}\right) + A_2 \cdot \left(1 - e^{\left(\frac{-x}{t2}\right)}\right) \tag{1}$$

Y = cumulative volatilization [% of applied]
A_1 = parameter A_1
A_2 = parameter A_2
t_1 = 1st half-life
t_2 = 2nd half-life
x = time after application [h]

The considerably lower volatilization of ^{14}C-FEN in experiment FEN-EC2 as compared to FEN-EC1 can be explained by the different climatic scenarios. The air temperature was about 9° C higher in experiment FEN-EC1 during the first 24 h (Table II, Figure 2) than in FEN-EC2. Generally, the major part of volatilization takes place in this period due to a weak adsorption/bonding of the pesticide on the leaf sur-

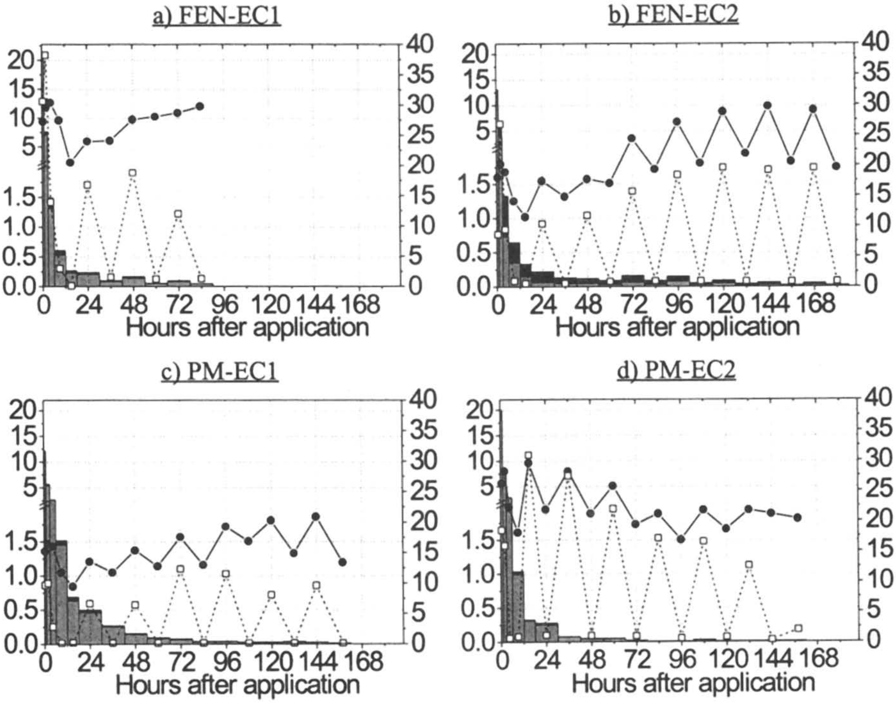

Figure 2. ^{14}C-volatilization rates of [phenyl-UL-^{14}C]fenpropimorph and [phenyl-UL-^{14}C]parathion-methyl after application onto dwarf beans. ▨ Volatilization rate of a.i. [% h^{-1}] (left axis), ■ volatilization rate of metabolites [% h^{-1}] (left axis), —●— air temp. [°C] (right axis), —□— irradiation [W m^{-2} 10^{-1}] (right axis), climatic parameters are averages within the air sampling intervals.

face. According to our own measurements, the air temperature corresponds very well to leaf surface temperatures. The high temperature sensitivity of fenpropimorph volatilization has also been observed in other wind tunnel experiments *(41)*.

In the replicate experiment FEN-EC2, where the activated carbon filter was removed (Table II), many more metabolites were measured in the air samples as compared to FEN-EC1 (Figure 2). This indicates, that indirect photolysis on the leaf surfaces plays an important role in the fate of fenpropimorph after plant application. Fenpropimorph does not show direct photolysis *(35)*, but it is sensitive to oxidation in general and especially for OH· radical attack *(42)*. Generally, directly measured volatilization rates of fenpropimorph in field experiments *(43-45)* were much lower as compared to laboratory experiments *(32,41)*. On the other hand, indirect methods (disappearance, measurement of residues) indicated high losses, e.g. in a lysimeter study, where fenpropimorph was applied to winter wheat. Only about 30 % AR was recovered 56 d after application, indicating that about 70 % of the applied fenpropimorph or its metabolites had been lost undetected via the atmosphere *(46)*. All this might be explained by a rapid decomposition of fenpropimorph in the field due to indirect photolysis, which is much less probable in indoor volatilization chambers due to lack of UV-B light and radicals.

However, in other wind-tunnel experiments *(32)*, measuring the volatilization of ^{14}C-FEN from summer barley under simulated outdoor conditions in the laboratory, 46.1-60.3 % AR volatilized in total within 96 h. This is in good agreement with the observed volatilization of ^{14}C-FEN presented in this paper.

On the basis of volatilized ^{14}C-activity, ^{14}C-PM showed a slightly higher volatilization potential (PM-EC1+2 about 60 % AR in total) than ^{14}C-FEN (37-55 % AR in total), especially for the WP formulation (73 % AR in total) (Figure 2). On the basis of volatilized a.i., differences were negligible (with the exception of FEN-EC2). Especially for PM-WP, the higher volatilization level was caused by a high amount of volatilized 4-nitrophenol during the first day of the experiment. In other experiments (Ophoff 1996, personal communication), no significant differences in the volatilization of a WP or EC formulation of ^{14}C-PM were observed.

Generally, volatilization of ^{14}C-PM from 7-week-old dwarf beans corresponds very well with other wind-tunnel experiments under standardized conditions; volatilization of ^{14}C-PM from dwarf beans decreased with increasing plant age and ranged from 45 % AR in 24 h (8-week-old dwarf beans) to 68 % AR in 24 h (4-week-old dwarf beans) *(47)*.

Both for ^{14}C-FEN and ^{14}C-PM, ^{14}C residues in plants were higher with experiments having a lower overall volatilization (Table IV). It is assumed that plant uptake of pesticides is a process antagonistic to pesticide volatilization *(48)*.

Volatilization of Terbuthylazine and Parathion-methyl from Bare Soil. Volatilization from bare soil was low, only 2.3 % of the applied ^{14}C-PM and 0.5 % of the applied ^{14}C-TER volatilized in the 19-day wind-tunnel experiment DLO-1. 1.1 % of the applied ^{14}C-TER volatilized as an unknown terbuthylazine metabolite (Figure 3). Volatilization of soil applied fenpropimorph (non-^{14}C-labeled, Table III) was below the detection limit in all wind-tunnel air samples (detection limit on DAD-HPLC was about 50 ng). Volatilization of ^{14}C-PM was much lower as compared to plant application (see above). This has already been described for many pesticides, since soil adsorption reduces effec-

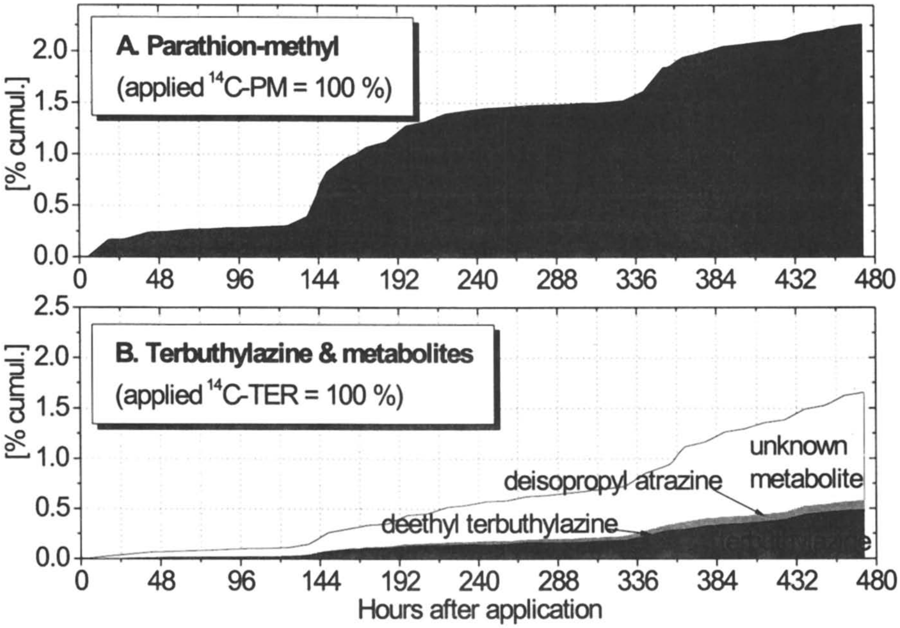

Figure 3. Cumulative volatilization of parathion-methyl, terbuthylazine, and its metabolites after application onto bare soil in the wind tunnel (stacked data).

tively the volatilization potential of a pesticide. A low volatilization of soil-incorporated parathion-methyl (0.25 % in 29 d) has been described by Spencer et al. *(33)*.

In the wind-tunnel experiments, the volatilization rates (Figure 4) were very low (^{14}C-PM: max. 0.054 % a.i. h^{-1}, ^{14}C-TER: max. 0.004 % a.i. h^{-1}) and showed a clear diurnal rhythm for both compounds. The experiment was started in a warm and dry summer period, resulting in an initial soil moisture content of only about 3 % within the first mm of soil. Because of the very strong adsorption of pesticides on air-dry soil *(3)*, the initial volatilization rates were low, increasing considerably with remoistening of soil after rainfall events (Figure 4). The log volatilization rates of ^{14}C-PM and ^{14}C-TER followed the pattern of soil moisture in the wind-tunnel soil remarkably closely (Figure 4) as already described for several pesticides *(49-51)*. Both pesticides have Henry's law constants < 10^{-5} (Table I) and are thus category III chemicals (non-volatile) according to a classification by Jury et al. *(52)*. Consequently, their volatilization rates are strongly dependent on evaporation of soil water (concentration at the soil surface due to mass flow). This results in a diurnal rhythm of ^{14}C-PM and ^{14}C-TER volatilization, i.e. higher volatilization rates during the day due to higher temperatures.

At the end of the experiment, in total, 93.3 % AR (= ^{14}C-PM + ^{14}C-TER + metabolites + non-extractable residues) was found in the lysimeter soil (Table IV). The characterized pesticide residues are summarized in Figure 5. ^{14}C-TER residues (69 % a.i.) were considerably higher than fenpropimorph (20 % a.i.) or ^{14}C-PM residues

(5 % a.i.). Since volatilization losses are generally low it can be concluded that the major part of the applied compounds was lost via mineralization in soil.

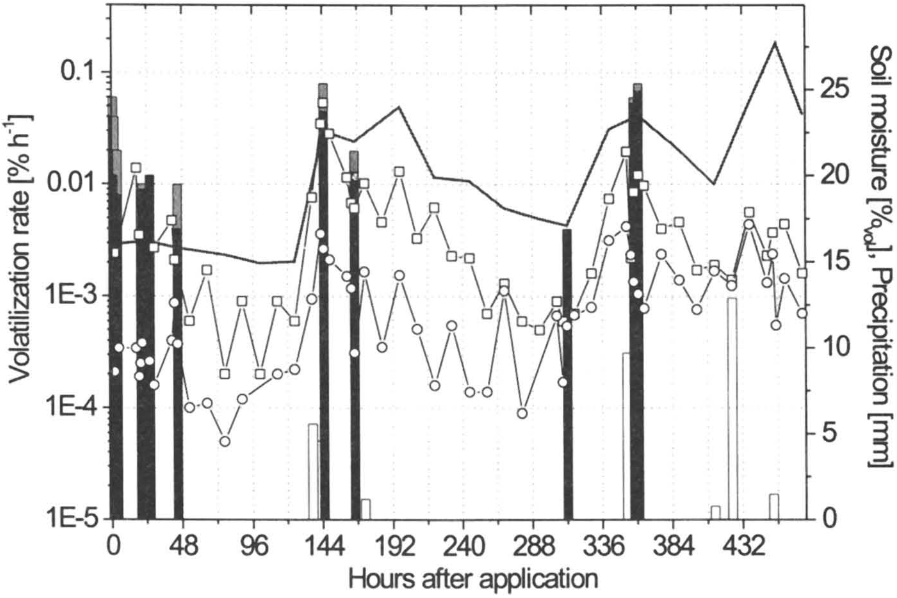

Figure 4. Comparison of parathion-methyl and terbuthylazine volatilization rates (VR) in the field and in the wind tunnel. Field data are averages of the aerodynamic and Bowen ratio methods. —□— VR ^{14}C-PM wind tunnel, —○— VR ^{14}C-TER wind tunnel, ▨ VR parathion-methyl field, ■ VR terbuthylazine field, — soil moisture in wind tunnel, ☐ precipitation.

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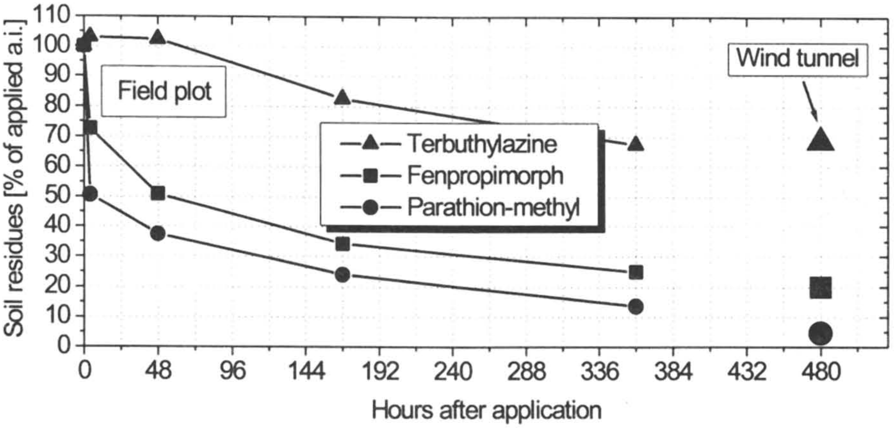

Figure 5. Experiment DLO-1 (bare soil): pesticide residues in field and lysimeter soil (0-10 cm).

Volatilization of Clopyralid. Volatilization of ^{14}C-CLO was low in both wind-tunnel experiments and amounted to 0.5 % AR (CLO-1, oil-seed rape) and 1.9 % AR (DLO-2, sugar beet), corresponding to 0.03 and 0.7 % volatilized ^{14}C-CLO (Figure 6). Even lower volatilization rates can be expected, when the application of clopyralid is carried out at the typical growth stage used in practical farming (BBCH 31-35), because then more active ingredient reaches the soil. The difference in the two experiments can again be explained as a temperature effect, a 40-45 % higher soil coverage in experiment DLO-2, and is probably not caused by the different plant surfaces. Ambient temperature in experiment CLO-1 was about 13 K lower than in experiment DLO-2 (Table II). In addition, in experiment CLO-1 a relatively high amount of ^{14}C-CLO reached the soil, which is less subject to volatilization, due to incomplete soil coverage by the young rape plants.

In both experiments, the amount of volatilized metabolites (NIR = non-identified radioactivity (metabolites)) was larger than volatilized ^{14}C-CLO itself (Figure 6), especially at the beginning of the experiment (Figure 7). Due to the low volatilization rates in experiment CLO-1, most of the residues in the air samples were below the detection limit of ^{14}C-CLO, and thus ^{14}C-activity had to be designated as non-identified.

Measured volatilization rates of ^{14}C-CLO in the wind tunnel were generally low (CLO-1: < 0.01 % h^{-1}, DLO-2: 0.01-0.03 % h^{-1}, Figure 7). They followed a diurnal rhythm in experiment DLO-2, probably due to changes in irradiation and surface temperature. In experiment CLO-1 volatilization of ^{14}C-CLO and NIR started at relatively

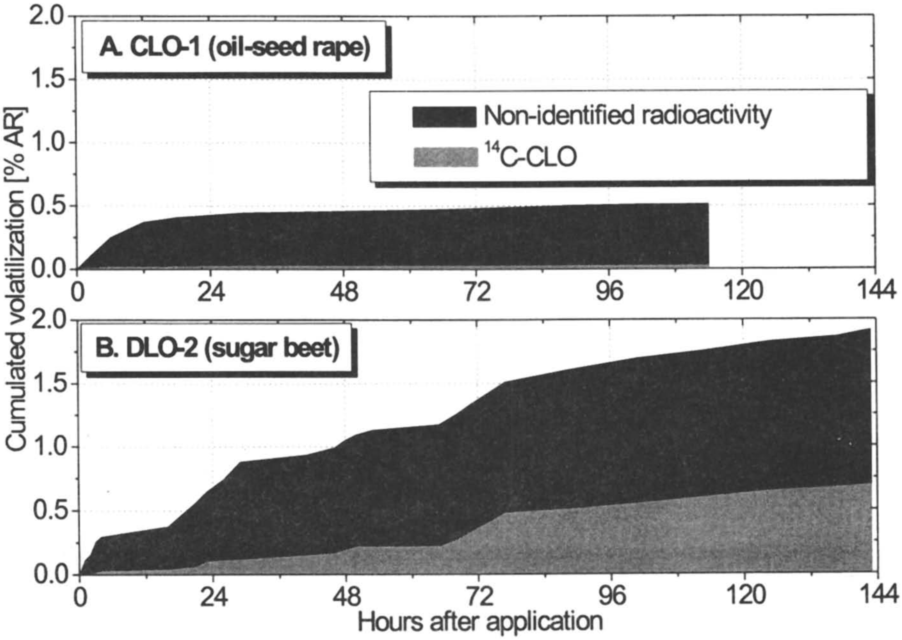

Figure 6: Cumulative volatilization of clopyralid and its metabolites after application onto oil-seed rape and sugar beet in the wind tunnel (stacked data).

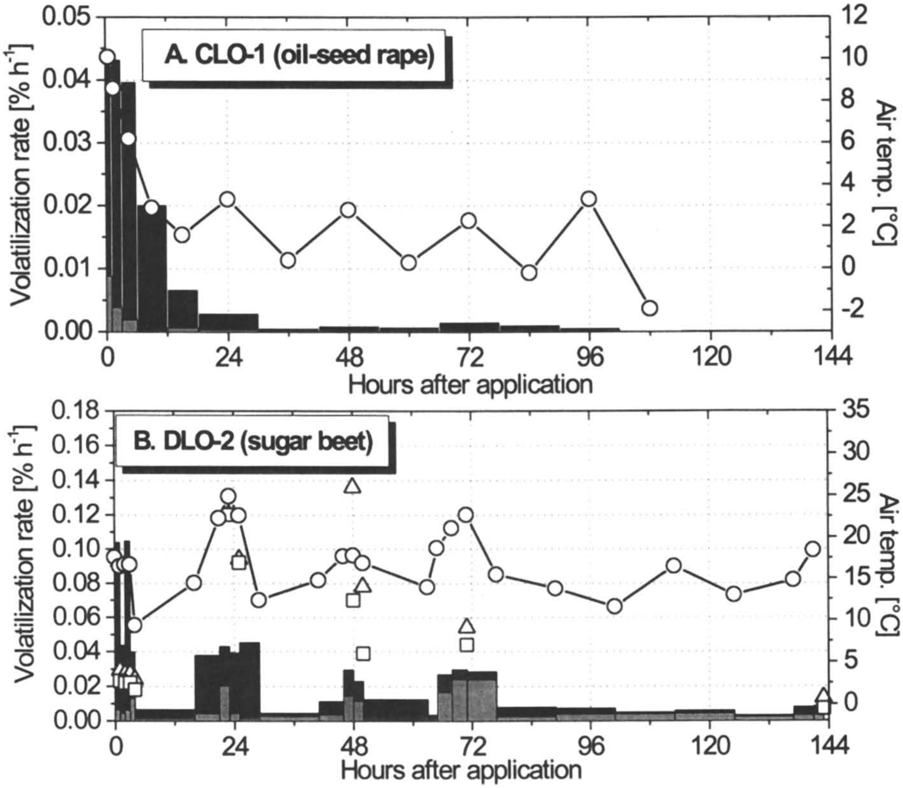

Figure 7. Comparison of clopyralid volatilization rates (VR) in the field and in the wind tunnel (stacked data). ▨ VR ^{14}C-CLO wind tunnel, ■ VR NIR wind tunnel, △ VR clopyralid field (aerodynamic method), ☐ VR clopyralid field (Bowen ratio method), —O— air temperature (average in air sampling intervals).

high rates and decreased constantly to a much lower level, which is typical of pesticide volatilization from plant surfaces (see above). In experiment DLO-2, the kinetics of volatilization was quite unusual in terms of volatilized unchanged ^{14}C-CLO, since the highest volatilization rates of ^{14}C-CLO were measured in the middle of the experiment about 72 h after application. ^{14}C-volatilization rates (^{14}C-CLO plus metabolites) showed the more typical pattern with high volatilization rates at the beginning, falling to much lower rates at the end of the experiment. But volatilization rates decreased only slightly during the course of the experiment from 0.1 % AR h^{-1} to 0.01 % AR h^{-1} (Figure 7B). The metabolite pattern changed considerably during the course of the experiment DLO-2. Besides clopyralid, two unknown metabolites were separated in the air samples. No clopyralid methyl ester was detected above the detection limit of 0.5 pg in any air sample. Metabolite 2 occurred mainly at the beginning of the experiment (0-4 h after application), whereas metabolite 1 was mainly present in air samples obtained 26-50 h after application.

In both experiments, the major fraction of radioactivity was detected in the plants (CLO-1: 53 % AR, DLO-2: 83 % AR) indicating a rapid uptake of ^{14}C-CLO. The extractability of ^{14}C-residues in leaves was very high in both experiments (> 90 %) and the residues were determined to be largely unchanged ^{14}C-CLO. The large amount of ^{14}C (23 % AR) in the beet roots (DLO-2) may be due to adsorption of ^{14}C-CLO on the surface of the roots, but more likely to translocation of ^{14}C-CLO or its metabolites from the treated leaves. The chemical nature of ^{14}C in the beet roots has not been determined. Due to an incomplete coverage of the soil surface with oil-seed rape in experiment CLO-1 (Table II), a considerable amount of ^{14}C reached the soil during application, which amounted to 44 % AR found in the soil at the end of the experiment. In the experiment with sugar beets (DLO-2), where the soil was almost completely covered, 12 % AR was found in the soil.

Comparison of Wind Tunnel vs. Field. Simultaneous field experiments were conducted together with experiments DLO-1 and DLO-2 (Table III). The wind tunnel climate deviated only slightly from the field climate in terms of air temperature, soil/plant temperature, and wind speed. In the bare soil experiment DLO-1, only for TER did the measured initial amount in soil (4 hours after application) match well with the calculated theoretical field dose (= 100 %) (Figure 5). The amounts of FEN (72.6 %) and PM (50.5 %) were considerably lower than the theoretical value, probably due to rapid chemical conversion, e.g. photodegradation. By the end of the experiment, the soil residues in the field had decreased constantly to 24.9 % (fenpropimorph), 13.6 % (parathion-methyl) and 67.4 % (terbuthylazine) and matched well with the residue situation in the lysimeter soil of the wind tunnel (Figure 5), considering a sampling date 5 d later.

Similar to the observations in the wind tunnel, parathion-methyl volatilization in the field experiment was always higher than the terbuthylazine volatilization, and volatilization rates assimilated over time. The kinetics in both test systems seem to follow the same pattern, influenced by remoistening during rainfall events. In contrast to the soil residue levels, measured field volatilization rates were generally about one order of magnitude higher than in the wind tunnel. Due to the complete radioactivity balance and the confirmation of the aerodynamic method by the Bowen ration method and vice versa, it can be assumed that both test systems measured correct volatilization rates **within the respective system**. Some differences between the two systems, however, are listed in order to explain the different results:

- With the wind tunnel application, about 4.5 times the application volume of water (900 L ha^{-1}) was used as compared to the field application (200 L ha^{-1}) (Table III), which could lead to a deeper penetration and translocation of the pesticides into the soil.
- This effect was enhanced even more by the type of irrigation performed in the wind tunnel, using one full cone nozzle in the lid. The irrigation events had a much higher intensity (2 mm min^{-1}) than typical precipitation in the field, leading in addition to puddling and compaction of the lysimeter soil. The reducing effect of increasing bulk density on pesticide volatilization has been described earlier *(53)*.
- Possibly the most important effect was the constantly lower soil moisture (measured by TDR in 2 cm soil depth) in the wind tunnel (mean: 19.9 %$_{vol}$) as compared to the

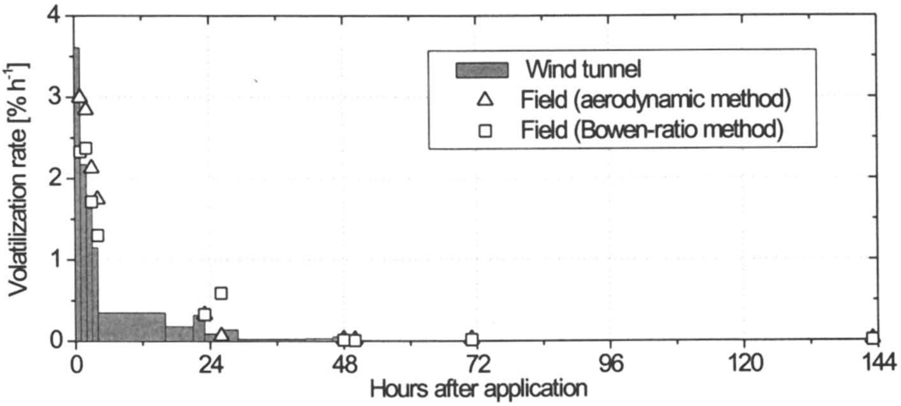

Figure 8. Comparison of fenpropimorph volatilization rates (VR) in the field and in the wind tunnel.

field (mean: 21.3 $\%_{vol}$), although the cumulated evaporation potential of water was calculated *(54)* as slightly higher in the field (+10 %). The strong influence of soil moisture content on pesticide volatilization is shown in Figure 4. However, on sunny days in the field, the soil moisture in the very top millimeters of soil, where the pesticide residues are located, was much lower than TDR measurements in 2 cm soil depth.

In contrast to the bare soil experiment, the volatilization rates of clopyralid and especially fenpropimorph in the field experiment were in good agreement with the wind-tunnel measurements (Figures 7B and 8). During the first 4 h after application, the clopyralid volatilization rate was just below the detection limit of 0.027 % h^{-1}, which corresponds quite well with the volatilization rates measured simultaneously in the wind tunnel (about 0.01 % h^{-1}). At 68 h as well as 142 h after application, the field data was just higher by a factor of two. There was a larger deviation, i.e. a much higher volatilization rate in the field as compared to the wind tunnel, between 26 and 50 h after application with the occurrence of the unknown metabolite 1, which was not present in the other air samples. It might be assumed that the GC method used for field air samples, which included a derivatization to clopyralid methyl ester, is not only specific to clopyralid but also to at least one (unknown) metabolite, causing a higher reading for clopyralid (in the form of clopyralid methyl ester). In the analytical methods used in the wind tunnel experiment, no derivatization of clopyralid was practiced.

Fenpropimorph was applied together with clopyralid (Table III). An almost perfect match of volatilization rates was measured for fenpropimorph in terms of rates and kinetics (Figure 8). In total, 16 % volatilized in the wind tunnel. Since fenpropimorph was not radiolabelled in the wind tunnel either, metabolites could not be analyzed. It cannot be excluded that a major portion of the applied fenpropimorph was volatilized in the form of metabolites, since in this experiment the activated carbon filter was removed from the air inlet and side walls of the tunnel were replaced by UV-transparent glass.

In experiment DLO-2, the clopyralid and fenpropimorph residues in sugar beet leaves decreased constantly during the field experiment. Field and wind-tunnel results also corresponded well *(29)*. At the end of the experiment, 4.3 % of the applied ^{14}C-CLO (field: 2.7 %) and 5.3 % of the applied fenpropimorph (field: 12.8 %) were detected in the sugar beet leaves of the wind tunnel.

Conclusions

Wind-tunnel experiments employing ^{14}C-labelled pesticides yielded complete radioactivity balances in a semi-field experimental setup. Comprehensive data are obtained regarding pesticide residues and metabolites in air, plant, soil and water (leachate). In wind-tunnels, field conditions in bare soil experiments are more difficult to simulate than in plant experiments due to the sensitivity of volatilization to some parameters which are hard to control, e.g. irrigation intensity, soil density, soil moisture (profile), evaporation, etc.

For bare soil experiments, soil moisture and evaporation are confirmed to be very important factors influencing pesticide volatilization. Pesticide volatilization from plants is generally much higher and mainly influenced by air temperature. Due to the large differences in pesticide volatilization from plants and soil, the amount of pesticide reaching the soil or plant in agricultural use is of much more importance than any climatic factor.

Besides volatilization, direct and indirect photolysis has to be taken into account when studying the behavior of pesticides under (semi-)field conditions since pesticides are mainly sprayed directly onto the soil (pre-emergence) and plants (post-emergence) and hence exposed to UV light and atmospheric radicals. Little is known about photolytical processes on plant and soil surfaces, but there are some examples showing that these processes are different from the photolysis studied in solution *(55,56)*.

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Chapter 3

Lysimeter Study of Imidacloprid After Seed Treatment of Sugar Beet in Two Crop Rotations

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According to German Lysimeter Guideline the leaching behavior of [imidazolidine-4,5-^{14}C] imidacloprid (insecticide) and its degradation products is investigated under practice-relevant field conditions. Imidacloprid treated sugar beet seed was sown in two undisturbed soil monoliths (1.0 m^2 surface area, 1.1 m depth) of sandy loam on April 1991 and 1994. The application rate was 1.3 mg active ingredient/pellet (9 pellet/m^2) corresponding to about 120 g/hectare each. In the other years cereals were grown. Data/results were gathered during the five years on 1) weather, 2) occurance, volumes, radioactive residues of leachate, 3) yields, residues in the harvested crops, 4) distribution of residues in the soil monoliths at the end of the study, 5) material balance and calculation of portion mineralized to $^{14}CO_2$. This study confirms the low mobility of imidacloprid and its degradation products in soil under practice-relevant field conditions. Following the use of imidacloprid in the recommended manner the possibility of contamination of deeper soil layers and groundwater can be excluded.

Plant protectants can be examined for their leaching potential in soils by various laboratory studies. In case of the systemic insectice imidacloprid some physical-chemical properties (i.e. solubility in water and Koc-values) and its moderate degradability in soil indicated a leaching potential. On the other hand, column leaching and field studies as well as a 2 year lysimeter study (*1*) showed no leaching of imidacloprid into deeper soil layers. Therefore, the objective of this lysimeter study was to get further data on the potential long-term leaching behavior of imidacloprid and its degradation products by investigating its use as a seed dressing in a sugar beet/cereal crop rotation in which sugar beet was grown twice in 6 years.

In The Lysimeter Concept; Führ, F., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 1998.

Materials, Methods and Test Conditions

Test substance. The study was conducted with [imidazolidine-4,5-^{14}C] imidacloprid (Figure 1). The specific radioactivity was 4.59 MBq/mg (124 µCi/mg) and the radiochemical purity determined by TLC and HPLC was >98%.

Reference standards. Many reference standards covering possible transformation products of the test substance were available. However, metabolism and leaching studies of imidacloprid in soil indicated that the parent compound is expected to be the relevant residue in soil, together with the bound residues.

Information on the lysimeter. This semi-field study running under GLP and according to official Guidelines (*2*) was conducted with two undisturbed soil monoliths (1.0 m^2 surface area; 1.1 m depth) of sandy loam (Eutric Cambisol) taken from field plot AXX of the Experimental Farm Laacherhof of Bayer AG, Monheim (FRG) in April 1990. Initially, they were installed above ground in the "lysimeter hall" of the Metabolism Institute. Then 11 months after 1st application of [^{14}C] imidacloprid, the two lysimeter systems were transferred into a newly built lysimeter facility and installed at ground level. Details of test system, type of soil and location of the Bayer lysimeter facility have already been published (*3*).

The leachate was collected in stainless steel containers which were emptied every 2 weeks (more frequently, if necessary). The sample volume was determined gravimetrically. The net radioactivity ($TRR_{alkaline}$) was determined by liquid scintillation counting (LSC) of each of three 10 mL aliquots after addition of 100 µL 1 M NaOH to ensure retention of dissolved ^{14}C-carbonates. The TRR_{acidic} was determined by LSC of each of three 10 mL aliquots after addition of 100 µL of 18% HCl to release of $^{14}CO_2$ from the solution. The arithmetic means were used for calculations. Sum fractions (i.e. annual leachates, AL) were prepared by mixing 10% of all the individual leachates which were analyzed by radio-TLC (for methods see later).

No soil sampling was conducted during the period that the leachates were collected. In May 1996 the five top soil layers each 10 cm deep were taken from the complete area of the lysimeters and mixed in a dust-tight concrete mixer for about 1 hour. Five subsamples from each mixed layer were taken and five 1 g portions of each were combusted for determination of ^{14}C-residues. Five soil cores of the deeper layers were taken using an electric soil corer (∅ = 8 cm^2) and five 1 g portions of each were combusted in order to determine the ^{14}C-residues. The total weight/layer was calculated from the weight of the cored portion. The soil corer did not reach the gravel in the tray. An individual sample of about 550 g was taken after the lysimeter was lifted out of the unit in November 1996. The gravel was extracted by 200 mL acetonitrile/0.1 N HCl 1:1 (v+v) for 2 hours and the extract was radioassayed (3 aliquots each).

The extractable radioactivity in the soil was determined to a depth of 80 cm. Two 25 g aliquots/layer each containing the mean ^{14}C-residue of the respective layer were hot-extracted in a ®Soxtec apparatus with 40 mL of methanol (1 hr reflux, 0.5 hr rinsing). An aliquot of 500 µL (in the case of top soil layers) or 1,000 µL (in the case of lower soil layers) of the crude extracts was spotted by Linomat IV (Camag Co.) in bands of 1 cm directly onto silica gel 60 F_{254} pre-coated TLC plates (Merck Co.). The solvent systems ethylacetate/2-propanol/water 65/23/12 (v+v+v) and chloroform/

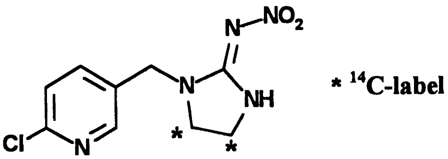
Cl
N
N
NH
N
NO_2
*
*
* ^{14}C-label

Figure 1. Structure of Test Substance

methanol/acetic acid/water 65/25/3.5/3.5 (v+v+v+v) were used for separation. Detection and evaluation was performed by radio-TLC-Scanner RITA 68,000 (Raytest Co.; lower limit of determination ≈2 Bq/appl. volume or /spot), later by Bio-Imaging Analyzer BAS 2000 (Fuji Co.; lower limit of imidacloprid determination about 0.005 µg/L leachate or 0.005 µg/kg soil).

Application of test compound. On April 3, 1991 each 25 µL of a dichloromethane solution of [^{14}C]imidacloprid was applied directly to sugar beet pellets lying in three rows in the soil monoliths. The rate was 1.3 mg a.i./pellet with 9 pellets/m^2 corresponding to 117 g a.i./hectare. The 2nd sugar beet treatment corresponding to 126 g a.i./hectare was applied similarly on April 27, 1994. In the first treatment 53.95 MBq/lysimeter was applied (≡100% in the testing period of 3 years) and in the second 58.72 MBq/lysimeter. In total 112.67 MBq (≡100% for the last 24 months of study and the total testing period of 5 years plus 1 month) was applied to each lysimeter.

Cultural practices and cropping. All the agronomic and maintenance activities (fertilization, crop protection and other measures) within the lysimeters and the surrounding field plot (*3*) were conducted and documented by a gardener. The main goal of the activities, which were performed in compliance with good agricultural practice, was obtaining crop growing conditions and yields which would be expected on a local farm. Data about cropping, vegetation periods and crop yields are presented in Table I.

Test conditions. The relevant climatic data were recorded at the weather station of the Bayer Experimental Farm Laacherhof, Monheim, located about 1 km away. Specimen weather data from 1966-1995 are listed (Table II) in order to characterize the test location and to compare it with the conditions in the course of the lysimeter study. The conditions generally required for a lysimeter study (*2*) were maintained during the period from April 1991 to April 1996. Cumulative curves of precipitation & irrigation and the measured leachate portions are shown in Figure 2.

The combination of using a seed treatment (point source), the method of treating the sugar beet pellets (a.i. not incorporated) and the sandy soil used in the lysimeters were considered to produce a worst case situation for testing the leaching potential of imidacloprid. As usual for field testing conditions, the weather was quite different from year to year. Nevertheless, precipitation & irrigation on average exceeded by 12 mm/a the value of 800 mm/a required for lysimeter studies (*2*). The total leachate volumes (Figure 2) varied in the expected range, each reflecting the actual crop growing and weather conditions. The duplicates were closely comparable. Within the total testing period of 5 years plus 1 month the leachate amounted to 26% of total precipitation plus irrigation. Leachate volumes as well as crop yields harvested from the lysimeters indicated good crop growing conditions and a normal water balance in the soil monoliths.

Results and Discussion

Leachates. The net radioactive residues ($TRR_{alkaline}$) measured in all individual leachates and expressed as µg a.i.-equivalent/L are shown in Figure 3. In general, the

Table I: Cropping, Yields and ^{14}C-Residues in Crops

Crop	*Period of growth*[1] *[days]*	*Elapsed time*[2] *[days]*	*Crop yield (f wt.) [kg/m²]*	*^{14}C harvested/ lysimeter [% appl.]*[3]	*Total ^{14}C residue (a.i. equivalent) [mg/kg f wt.]*
1st (target): sugar beet	224	224			
- tubers			7.4	0.72	0.011
- leaves			4.2	0.41[4]	0.061
2nd: wheat	265	489			
- grains			0.8	0.04	0.006
- straw			0.7	0.02[5]	0.039
chaff			0.3	0.05	0.025
3rd: barley	281	819			
- grains			0.7	<0.01	0.008
- straw			0.6	<0.02[5]	0.013
- chaff			0.2	<0.01[5]	0.015
Phacelia	not harvested intermediate crop used as organic fertilizer				
4th (target): sugar beet	166	166 (1,286)			
- tubers			7.6	0.61	0.020
- leaves			5.7	0.54[4]	0.106
5th: wheat	268	449 (1,569)			
- grains			0.9	0.03	0.008
- straw & chaff			1.1	0.40[5]	0.075
6th: barley	203	733 (1,853)			
- forage			1.8	0.33	0.046

The listed values are the means of duplicates.

[1]: i.e. period of crop exposed to ^{14}C.

[2]: from last ^{14}C treatment until harvest; values (XX) from 1st treatment until harvest.

[3]: % of ^{14}C applied until that time.

[4]: only 2/9 of yield was harvested from the lysimeters.

[5]: only 1/10 of yield was harvested from the lysimeters.

Table II: Long-term weather characteristics of test location

Parameter	*Long-term annual average values* 1) *at test location*	*Deviation of measured* 2) *to long-term means*	
		Rainfall & irrigation [mm]	
Annual rainfall [mm]	745		
		1st year:	+17
Monthly rainfall$_{max}$ [mm]	Jun: 78.1	2nd year:	+109
Monthly rainfall$_{min}$ [mm]	Feb: 42.7	3rd year:	+179
		4th year:	+239
		last period:	-205
		total:	+339
		1st year:	+0.5
Annual air temperature [°C] at 2 m above ground level	10.0	2nd year:	+0.9
		3rd year:	+0.3
Monthly avg$_{max}$ [°C]	Jul: 18.4	4th year:	+1.4
Monthly avg$_{min}$ [°C]	Jan: 2.6	last period:	0.0
		total:	+0.6
Annual wind velocity [m/sec] at 2 m above ground level	2.5	total:	-0.2
Annual soil temperature [°C]:	9.5	total:	+0.4
- at 10 cm depth	9.5	total:	+0.4
- at 30 cm depth	10.3	total:	+0.6
- at 50 cm depth	10.7	total:	+0.9
- at 100 cm depth	10.6	total:	+0.7

soil temperatures were calculated using the daily values at about 7:30 AM each

1) : 1966 - 1995, except soil temperatures 1968-1995.

2) : respective values relevant for the lysimeter study in the specified period.

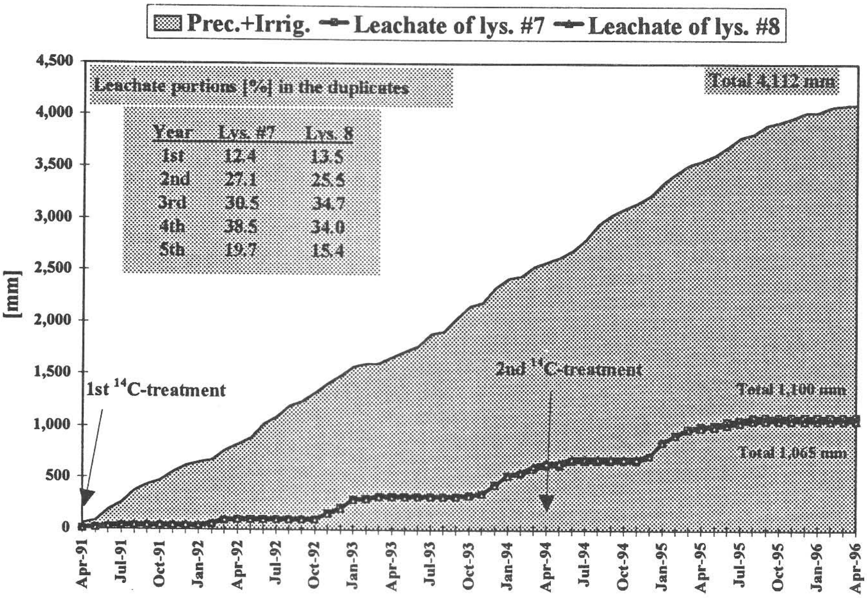

Figure 2. Cumulative Curves of Precipitation & Artificial Irrigation and Leachate Portions in the Duplicates

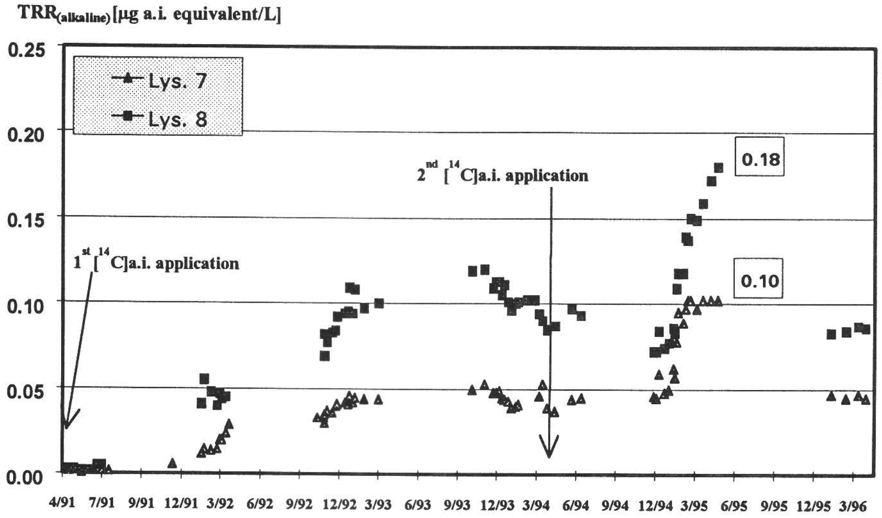

Figure 3. ^{14}**C-Content (TRR) in the Individual Leachates**

TRR in the leachates of lys. #8 was about twice that of lys. #7. However, the overall trends were similar.

Until Nov. 1993 (≈32 months after the first treatment) the ^{14}C-content increased slowly to a maximum of about 0.05 and 0.12 µg a.i. equivalent/L in lys. #7 and #8, respectively. No so-called preferential flow was observed. In the further period a slight decrease of ^{14}C-content was indicated, already. But later, the break through of ^{14}C resulting from the second treatment occurred and the TRR increased, again. The TRR_{max} (Figure 3) was reached after 48 and 50 months (lys. #7 and #8). Finally, the ^{14}C-content decreased to less than 0.05 (lys. #7) and less than 0.09 (lys. #8) µg a.i. equivalent/L.

The results of investigation of the mixed leachates are presented in Table III. The mean TRR_{acidic} was always less than 0.1 µg a.i. equivalent/L. Further, neither parent compound nor any known metabolite of imidacloprid could be detected via radio-TLC-analyses. If at all present, the concentration of parent compound must have been lower than 0.01 µg/L. The predominant portion of TRR_{acidic} contained in the leachates was unknown radioactivity, but all individual peak zones corresponded to less than 0.05 µg/L each. During the long study period it is plausible that a measurable portion of ^{14}C would be transported through the soil monolith into the leachate. This is evidence for the fact that the active ingredient imidacloprid participates in the natural carbon cycle of the soil. It is noteworthy that a quite low portion of total applied ^{14}C (only 0.2 and 0.4%) was leached through the soil monoliths #7 and #8 during the entire study period.

Recovered Radioactivity in Soil. The comparatively low mobility of imidacloprid and its metabolites in soil was supported by the measured distribution of ^{14}C in the processed soil monoliths (Figure 4). The majority of recovered radioactivity (≈93%) was still located in the three top soil layers, i.e. more or less the plow layer. The main portion of the TRR was not extractable (bound), whereas the main portion of extractable radioactivity was unchanged parent compound. The distribution of imidacloprid residues in the soil monoliths as well as the recoveries are presented in Figure 5. The quite low imidacloprid residues decreased from about 12 µg/kg FW of soil in the top layer to less than LOD (i.e. less than 0.005 µg/kg FW of soil) at 60-70 cm depth of soil.

^{14}C-Material Balance. The data for both lysimeters are given in Figure 6. The TRR as well as the ^{14}C taken off the systems in the harvested crops (Table I) were quite low (≈2.5%). The amounts of ^{14}C found in total leachate (≈0.3%) were much lower. The recovery of ^{14}C in the processed soil monoliths was comparable for both lysimeters and amounted to 43.8% and 44.3%. These figures indicate that 53.5% and 52.7% of ^{14}C initially applied to the soil monoliths had been mineralized and released into the air.

Conclusion

This study confirmed the low mobility of the parent compound imidacloprid and its degradation products in soil under practice-relevant field conditions. Following the use of imidacloprid in the recommended manner, the possibility of contamination of deeper soil layers and groundwater can be excluded.

Table III: Results (means of dupl.) of investigation of mixed leachate samples

Period	*Volume* *[L]*	*pH*	*$TRR_{alkaline}$* *[µg a.i.-equiv./L]*	*$^{14}CO_2$* *[%]*	*TRR_{acidic} [1]* *[µg a.i.-equiv./L]*	*A.i.* *[µg/L]*
1st year	98	7.1	0.020	--	0.020	n.d. [2]
2nd year	225	7.4	0.066	1.1	0.065	n.d. [2]
3rd year	301	8.0	0.075	3.9	0.072	n.d. [2]
4th year	357	7.6	0.089	6.9	0.083	n.d. [2]
5th year	102	7.4	0.088	8.3	0.081	n.d. [2]
Total	1,083	7.4	0.077	5.2	0.073	n.d. [2]

[1] % of $TRR_{alkaline}$; TRR = Total Radioactive Residue.

[2] not detected, i.e. <0.01 [µg/L].

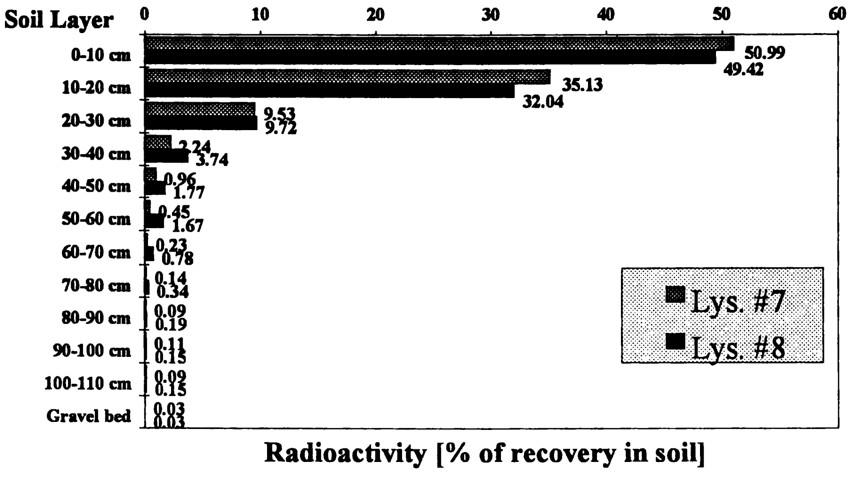

Figure 4. Distribution of ^{14}C-Content in the Soil Monoliths at Termination of the Study

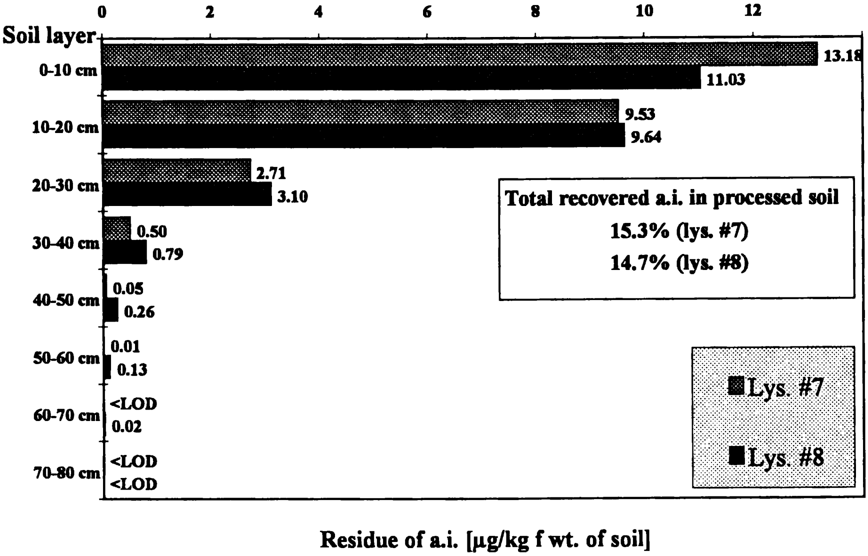

Figure 5. Content of ^{14}C-Imidacloprid in the Soil Monoliths at Termination of the Study

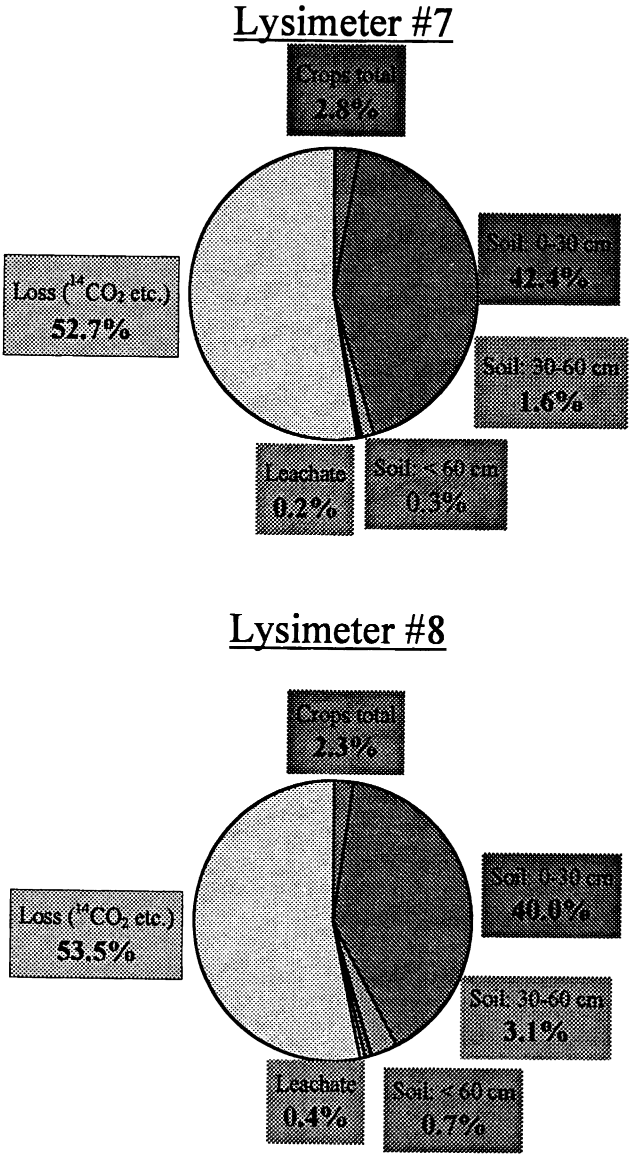

Figure 6. ^{14}**C-Material Balance for Lysimeter Study (% of Total Applied** ^{14}**C)**

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Chapter 4

Fate of the Herbicide Cinosulfuron in Rice Plant-Grown Lysimeters over Two Consecutive Years

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The fate of the herbicide cinosulfuron in rice paddies was elucidated by using lysimeters. Rice plants were grown on lysimeters treated with [^{14}C]cinosulfuron by the conventional method. During the growing period, the volatile chemicals, $^{14}CO_2$ evolved from the soil surface, and the leachate ^{14}C-radioactivity were measured. After harvest, the ^{14}C-radioactivity distributed in straw, ear without rice grains, chaff, and brown rice grains was also measured. When rice plants were cultivated for two consecutive years, the ^{14}C-radioactivity in straw was 47 ~ 116 times higher than that in brown rice grains in the first year, whereas in the second year, the amount decreased considerably, being still 38 ~ 51 times larger in the former than in the latter. The ^{14}C-radioactivity distributed down to the 30-cm soil depth was 89 ~ 92% of the original amount in the first year, and 60 ~ 71% in the second year. The ^{14}C-radioactivity leached gradually with time, totaling 0.5 ~ 0.6% of the original amount.

Lysimeter studies have been conducted to elucidate the fate of pesticides, including their persistence, degradation, mobility, and leaching characteristics in soil, and the uptake and translocation by a target plant, typically by using radiolabeled compounds because of their high sensitivity at extremely low concentrations *(1)*.

The sulfonylurea herbicide, cinosulfuron, 1-(4,6-dimethoxy-1,3,5-triazin-2-yl)-3-[2-(2-methoxyethoxy)phenylsulfonyl]urea, is highly active at a much lower rate than other herbicides against a wide range of broad-leaf weeds. It was registered as a granular formulation for use in rice paddies in Korea in 1994.

In general, sulfonylurea herbicides are mainly degraded by chemical hydrolysis and microorganisms in soil *(2-6)*. The higher soil pH and their water solubility, and the lower soil organic matter, the higher their mobility in soil is. Photodegradation and volatilization would be relatively minor dissipation processes *(7)*. Cinosulfuron was also more mobile in a soil column than two other sulfonylureas, bensulfuron-methyl or pyrazosulfuron-ethyl. Its mobility is dependent on soil texture, leaching rate and application rate *(8)*. Despite their relatively high mobility in soil, sulfonylurea

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herbicides do not seem to be a potential contamination problem in groundwater because of their low application rates, low toxicities, and the relatively rapid degradation and/or disappearance characteristics in soil *(3)*.

Since cinosulfuron is relatively a new chemical, it will be necessary to establish the standard for its safe use. For this purpose, lysimeters which can simulate the rice paddies in Korea were used for the conventional rice cultivation and the application of radiolabeled [^{14}C]cinosulfuron.

This research will be helpful for evaluating the environmental safety of cinosulfuron treated to rice paddy fields.

Materials and Methods

Lysimeter and Preparation of Soil Cores. Two cylindrical lysimeters were manufactured with stainless steel 8 mm in thickness. Their surface area was 0.25 m^2, the height 1.1 m, and the inner diameter 0.564 m. The undisturbed soil cores were obtained by pressing down the lysimeters on a rice paddy soil located at Bockdae-dong, Cheongju, Korea, with the aid of a fork-crane. The physico-chemical properties of the lysimeter soil layers are presented in Table I.

Table Ⅰ. Physico-chemical properties of each layer of the soil in the lysimeters

Soil depth (cm)	pH H_2O 1:5	C.E.C. (mmol(+)/ kg soil)	Organic matter (%)	Sand (%)	Silt (%)	Clay (%)	Texture
0 ~ 10	6.3	105.3	3.6	25.6	44.0	30.4	CL
10 ~ 20	6.9	102.8	2.7	21.1	48.2	30.7	CL
20 ~ 30	7.2	90.1	1.9	21.2	46.6	32.2	CL
30 ~ 40	7.4	102.4	1.0	20.5	41.4	38.1	CL
40 ~ 50	7.1	91.1	0.9	29.7	31.4	38.9	CL
50 ~ 60	6.7	76.2	0.7	28.8	40.9	30.3	CL
60 ~ 70	6.5	71.5	0.5	37.3	34.1	28.6	L
70 ~ 80	6.4	57.3	0.5	35.9	35.2	28.9	L
80 ~ 90	6.1	63.4	0.4	41.3	31.2	27.5	L
90 ~ 100	5.5	117.2	1.0	35.0	33.9	31.1	CL

Growing of Rice Plants. Prior to transplanting, the lysimeter soils were fertilized with N-P-K at the ratio of 150-90-110 kg/ha, except that 80% of the total nitrogen fertilizer was applied at the beginning and the other 20% applied at the earing stage. The 35-day-old rice seedlings (*Oryza sativa* cv. Akibare, Japan) were transplanted onto lysimeter soils on June 2, 1995. Twenty-seven seedlings (3 seedlings/hill × 9 hills) were transplanted on each lysimeter soil. Throughout the cultivation period, the soils were flooded, because rice culture in Korea usually needs submerged conditions almost until the harvest. Accordingly, during the dry season, water had to be replenished all the time, irrespective of the precipitation. After rice harvest, the lysimeters were kept open. The average monthly atmospheric and soil (10-cm depth from the surface) temperatures, and precipitation during the period from 1995 to 1996 are presented in Table Ⅱ and Ⅲ.

Table II. The monthly precipitation (mm) in Cheongju during the period of 1995-1996

	Month											
Year	1	2	3	4	5	6	7	8	9	10	11	12
1995	-	-	-	-	-	70.7	30.9	204.9	825.4	17.5	22.6	20.3
1996	27.9	4.2	98.4	28.6	36.8	255.8	170.5	128.6	11.2	67.7	77.2	22.5

Table III. The average monthly atmospheric and soil (10-cm depth from the soil surface) temperatures (℃) in Cheongju in 1995

Month	5	6	7	8	9	10	11	12
Atmospheric	-	23	26	27	19	12.9	2.6	-3.5
Soil	-	26	28	24	-	-	-	-

Application of [^{14}C]Cinosulfuron and Cultivation. [U-phenyl-^{14}C]Cinosulfuron (specific activity: 1.66 MBq/mg, purity: >96%) was supplied by Ciba-Geigy (Figure 1). The commercial granular formulation, Bujanon (0.08% cinosulfuron + 5% molinate + 94.92% adjuvant, etc.) in which cinosulfuron was replaced by [^{14}C]cinosulfuron as a tracer was applied onto lysimeter soils 22 days after transplanting.

To ensure the high concentration for studying the long-term behavior of cinosulfuron such as leaching and degradation in soil, and absorption and translocation by plants, [^{14}C]cinosulfuron applied onto the lysimeter soils was 3 times the real application rate (24 g ai/ha) recommended in Korea. The total amounts and radioactivity of cinosulfuron applied were 2.02 mg and 3.34 MBq in lysimeter I, and 2.01 mg and 3.33 MBq in lysimeter II, respectively. The ^{14}C-labeled cinosulfuron dissolved in about 10 mL of methanol and the formulation prepared without cinosulfuron were added to about 200 g soil. After the methanol was completely evaporated, the treated soil was uniformly spread on the submerged rice-grown lysimeter soil. Rice plants were grown for two consecutive years according to the same method as described above.

Leachates. The leachates through the lysimeter soils were collected in 2-L plastic containers, and the volume and radioactivity were measured weekly, if necessary. The radioactivity was measured by a liquid scintillation counter (LSC, PW 4700, Philips) with automatic quench correction. In order to examine the transformation of [^{14}C]cinosulfuron in the course of leaching through the lysimeter soil, about 5 L of the leachates through lysimeter II were collected from the 72nd to 75th week after application. The leachate was acidified down to pH 2 and partitioned into CH_2Cl_2. The organic phase was separated, concentrated to dryness, and redissolved in a small volume of acetone for autoradiography. TLC was performed, followed by autoradiography with the aid of a digital autoradiograph (Laboratory of Prof. Dr. Berthold GmbH, Germany). The developing solvent was a mixture of ethyl acetate-methanol (9:1, v/v).

Mineralization and Volatilization of Cinosulfuron during the Rice-Growing Period. $^{14}CO_2$ and volatile substances evolved from the [^{14}C]cinosulfuron-treated soil surface in the first year were trapped in 1 N NaOH and 0.1 N H_2SO_4, respectively, by the method of Lee et al. *(9)*, and their radioactivity measured biweekly by LSC.

Soil and Plant Sampling and Their Radioactivity. After harvest, the soil sample of each 5-cm layer was collected down to the 30-cm depth in the first year and 60-cm depth in the second year, with a soil core sampler attached to a stainless steel core of 5.05-cm diameter and 100 cm^3 volume. The samples were taken vertically from 3 random spots of the soil, and those of each layer were combined together, air-dried, and ground in a mortar for analysis.

The rice plants harvested were separated into straw, ear without rice grains, chaff, and brown rice grains, freeze-dried (Chem Lab. Instruments LTD., SB4, England), and pulverized with a cutting mill for the measurement of the radioactivity by combustion.

Each plant or soil sample (0.3g) was combusted with the Biological Oxidizer, OX-400 (R. J. Harvey Instrument Corporation, U.S.A.) to give $^{14}CO_2$ which was absorbed in the ^{14}C-cocktail (CARBO MAX PLUS LUMAC*LSC B. V., the Netherlands). The radioactivity was measured by LSC. The toluene cocktail was used for ^{14}C-radioactivity dissolved in organic solvents that were evaporated before the cocktail addition. The radioactivity of $^{14}CO_2$ absorbed in 1 N NaOH and volatile substances absorbed in 0.1 N H_2SO_4 were measured using Aquasol (Du Pont, NEN Research Products, U.S.A.) as a liquid scintillation cocktail.

Dehydrogenase Activity and the Number of Microbial Colonies in Lysimeter Soils. For comparison of the metabolic activity of microorganisms present in the lysimeter soil, before and after the growing of rice plants, the dehydrogenase activity of the soil was measured by the methods of Lee et al. *(9)* and Casida *(10)*.

For counting the number of microorganisms present in soil, 1 g of soil (on a dry weight basis) was added to 9 mL of sterile distilled water and shaken for 2 hours. The soil suspension was diluted adequately, 0.1 mL of which was spread on the nutrient broth medium and incubated at 30 °C for 48 hours. The colonies were counted with a colony counter *(11)*.

Extractable and Non-Extractable ^{14}C Soil-Bound Residues. Each 150 g of air-dried soil collected from every 5-cm layer of the lysimeter was exhaustively extracted with methanol. All extracts were combined and the combined radioactivity was measured. The extracted soil was then combusted to determine the non-extractable soil-bound residues.

Meanwhile, 5 g of the methanol-extracted soil samples were subsequently extracted with 0.1 M $Na_4P_2O_7$. The extracts were separated into fulvic and humic acid by acidification *(12)*. The radioactivity incorporated into fulvic and humic acid was measured with Aquasol. The extracted soils were combusted to determine the radioactivity remaining in the humin fraction.

Partition of Radioactivity of Soil Extracts between Aqueous and Organic Phase. To partition the ^{14}C-radioactivity in the methanol extracts of each soil layer between aqueous and organic phase, 10 mL of methanol extracts were evaporated by a bubbling air stream, added with 5 mL of distilled water, acidified down to pH 2 with 2 drops of 6 N HCl, and mixed homogeneously. Five mL of CH_2Cl_2 were then added to it and shaken vigorously. The radioactivity in the organic and aqueous phase was measured.

Results

As shown in Figure 2, the amounts of $^{14}CO_2$ evolved from the soil surfaces of lysimeter I and II during the cultivation period of 14 weeks after treatment of [^{14}C]cinosulfuron were 2.28 and 3.79%, respectively, of the originally applied ^{14}C-activity, while volatilization of the chemical from the lysimeter soil surfaces during that period was at the background level. The total amounts of radioactivity in the leachates from lysimeter I and II over the two years were 0.53 and 0.58%, respectively, of the original radioactivity applied, but those in the first year were negligible. The amounts of cinosulfuron equivalents contained in the leachates expressed as a mean concentration ranged from 0.14 (lysimeter I) to 0.20 μg/L (lysimeter II).

Table IV. Amounts of ^{14}C-radioactivity leached from the two rice plant-grown lysimeters treated with [^{14}C]cinosulfuron

Lysi-meter	Period (week)	Volume of leachate (mL)	% Original radioactivity	Original amount (mg)	Amount leached (mg)	Concentrations of cinosulfuron equivalent[a]/L (μg/L)
I	75	79,412	0.53	2.02	0.01	0.14
II	75	57,075	0.58	2.01	0.01	0.20

[a]Calculated on the basis of the specific ^{14}C-activity of the cinosulfuron

[b]^{14}C-Radioactivity leached from the lysimeter soils in the 1st year (1 ~ 20 weeks) was negligible.

Figure 3 is the autoradiogram showing that the CH_2Cl_2-partitioned ^{14}C-activity of the leachates from the lysimeter soil corresponds to the intact cinosulfuron. That is, some 42% of the leachate ^{14}C-activity represents the parent chemical and the rest might be more polar degradation products of cinosulfuron which can not be partitioned into CH_2Cl_2. The ^{14}C-activity distributed in different parts of rice plants after harvest is presented in Table V. It was detected in all parts such as straw, ear without rice grains, chaff, and brown rice grains up to the second year of cultivation, totaling 3.23 ~ 4.07% of the originally applied ^{14}C. Especially, the ^{14}C-activity in straw was reduced remarkably in the second year compared with the first year.

The dehydrogenase activity and the number of bacterial colonies of the lysimeter soils increased a little after the cultivation of rice plants (Table VI and VII), and the metabolic ^{14}C-activity of microorganisms in the soils was enhanced by addition of glucose and yeast extract to the soils as electron-donating substrates.

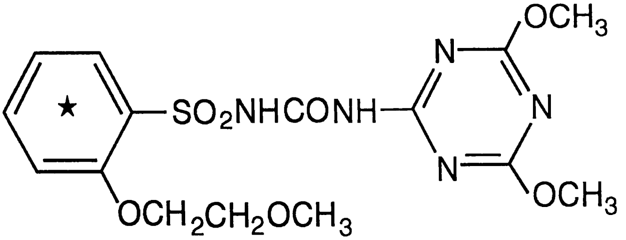

Figure 1. Structural formula and labeled position (*) of cinosulfuron, 1-(4,6-dimethoxy-1,3,5-triazin-2-yl)-3-[2-(2-methoxyethoxy)phenylsulfonyl]urea. Specific activity : 1.66 MBq/mg, Purity : >96%.

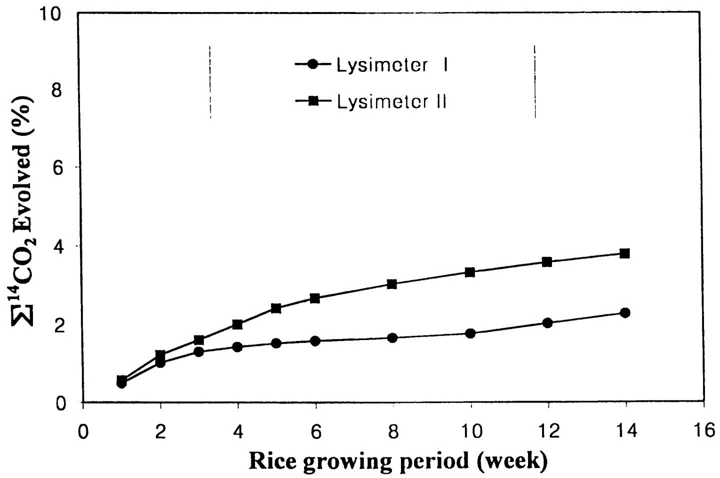

Figure 2. Mineralization of [^{14}C]cinosulfuron to $^{14}CO_2$ during the period of 14 weeks of the lysimeter experiment with rice plants. ^{14}C-Radioactivity applied = 100%.

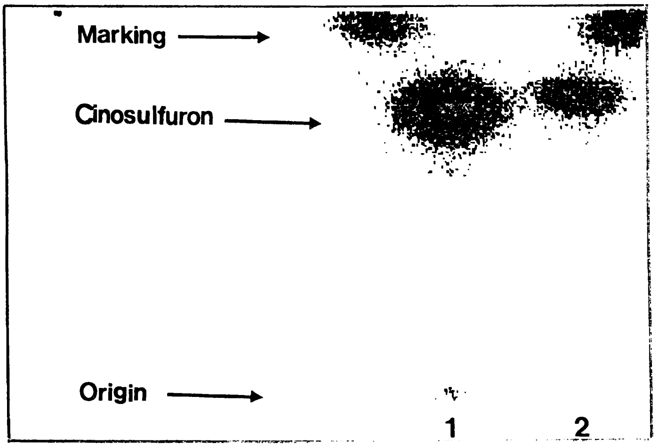

Figure 3. Autoradiogram of ^{14}C-activity (42%) which was partitioned into the CH_2Cl_2 phase after the leachate was acidified down to pH 2 and extracted. 1: Authentic [^{14}C]cinosulfuron, 2: ^{14}C-activity partitioned into the CH_2Cl_2 phase.

Table V. Amounts (%) of ^{14}C-radioactivity remaining in each part of rice plants grown on the lysimeter soils treated with [^{14}C]cinosulfuron.
Radioactivity applied =100%

Parts of rice plants	Lysimeter I		Lysimeter II	
	1st year	2nd year	1st year	2nd year
Straw	2.32 ± 0.26 (0.20 ± 0.03)[a]	0.75 ± 0.065 (0.08 ± 0.007)	2.82 ± 0.25 (0.25 ± 0.02)	1.01 ± 0.144 (0.13 ± 0.019)
Ear without rice grains	0.02 ± 0.007 (0.009 ± 0.001)	0.004 ± 0.000 (0.01 ± 0.001)	0.04 ± 0.01 (0.02 ± 0.01)	0.01 ± 0.001 (0.04 ± 0.003)
Chaff	0.06 ± 0.01 (0.04 ± 0.01)	0.03 ± 0.002 (0.03 ± 0.002)	0.06 ± 0.006 (0.05 ± 0.006)	0.05 ± 0.009 (0.05 ± 0.008)
Brown rice grains	0.02 ± 0.01 (0.003 ± 0.001)	0.02 ± 0.003 (0.004 ± 0.001)	0.06 ± 0.01 (0.01 ± 0.000)	0.02 ± 0.002 (0.01 ± 0.001)
Total	2.42	0.81	2.98	1.09

[a] Concentrations of cinosulfuron equivalent (μg/g) calculated on the basis of the specific ^{14}C-radioactivity (1.66 MBq/mg) of the cinosulfuron applied.

[b] Figures represent mean ± standard deviation of triplicates.

Table VI. Comparison of the dehydrogenase activity of the lysimeter soil treated with cinosulfuron before and after the 1st year of rice plant cultivation

Substrate	Formazan formed (mg/g soil[a])		
	Before cultivation (10~20cm soil depth)	After cultivation (15~20 cm soil depth)	
		Lysimeter I	Lysimeter II
Control	0.017	0.032	0.021
0.05M Glucose	0.043	0.048	0.054
0.1% Yeast extract	0.031	0.046	0.033

[a]Dry weight basis

Table VII. The number of bacterial colonies in the topsoil of the lysimeter before and after the 1st year of rice plant cultivation

Rice plant cultivation		Number of colonies (× 10^5 CFU[a]/g soil[b])
Before		2.88
After	Lysimeter I	3.60
	Lysimeter II	4.41

[a]Colony forming unit, [b]Dry weight basis

Table VIII represents the distribution of ^{14}C-activity expressed as cinosulfuron equivalents in different soil layers of the lysimeters after 1 and 2 years of [^{14}C]cinosulfuron application and cultivation of rice plants for 2 consecutive years. Most of the applied ^{14}C-activity (80.8 ~ 82.1%) remained in the 0 ~ 15 cm soil depth from the surface in the first year, but it decreased remarkably in the second year by the downward movement and degradation. The total ^{14}C-activity remaining down to the 60-cm depth from the surfaces of the lysimeter soils after 2 years was 74.7 and 76.8% of the originally applied ^{14}C-activity in lysimeter I and II. In Table IX, it can be seen that the non-extractable bound residues of [^{14}C]cinosulfuron increased with time and after the first year of cultivation, most of the ^{14}C-activity was incorporated into the fulvic acid fraction (82.5 ~ 93.6%), whereas after the second year, the ^{14}C-activity incorporated into the humin fraction increased (25 ~ 45.5%).

Table Ⅷ. Amounts of ^{14}C-radioactivity remaining in the different layers of the two lysimeter soils treated with [^{14}C]cinosulfuron after harvest. Radioactivity applied=100%

Soil depth	Lysimeter Ⅰ			Lysimeter Ⅱ		
(cm)	1st year	2nd year		1st year	2nd year	
	%					
0 ~ 5	33.81 ± 1.46	14.11 ± 0.32	-	22.28 ± 1.84	14.14 ± 0.78	-
5 ~ 10	36.37 ± 1.25	13.79 ± 0.32	-	38.09 ± 3.96	18.99 ± 0.76	-
10 ~ 15	10.59 ± 0.17	9.27 ± 0.67	-	21.68 ± 0.03	15.62 ± 0.31	-
15 ~ 20	5.33 ± 0.03	9.08 ± 0.22	-	3.64 ± 0.05	9.48 ± 0.29	-
20 ~ 25	3.62 ± 0.19	7.22 ± 0.70	-	2.42 ± 0.14	6.39 ± 0.54	-
25 ~ 30	2.50 ± 0.16	6.04 ± 1.16	-	1.15 ± 0.01	5.95 ± 1.59	-
30 ~ 35	-	-	5.58 ± 0.19	-	-	3.25 ± 0.29
35 ~ 40	-	-	4.07 ± 0.24	-	-	1.47 ± 0.18
40 ~ 45	-	-	3.67 ± 1.43	-	-	0.73 ± 0.06
45 ~ 50	-	-	1.05 ± 0.09	-	-	0.46 ± 0.07
50 ~ 55	-	-	0.43 ± 0.06	-	-	0.17 ± 0.06
55 ~ 60	-	-	0.37 ± 0.11	-	-	0.13 ± 0.11
		59.51	15.17		70.57	6.21
Total	92.22	74.68		89.26	76.78	

[a] Figures represent mean ± standard deviation of triplicates.

Table IX. Distribution of the ^{14}C bound residues in the lysimeter (II) soil after the rice plant experiment and repeated extraction with organic solvents.
Fulvic acid + Humic acid + Humin =100%

	Lysimeter soil layer from the surface (cm)	Non-extractable ^{14}C bound residues	Fulvic acid	Humic acid	Humin
		%			
1st year	0 ~ 5	51.38	82.52	1.21	16.28
	5 ~ 10	65.58	93.56	0.46	5.98
2nd year	0 ~ 5	76.67	52.07	2.46	45.48
	5 ~ 10	73.48	73.66	0.80	25.54

When the methanol extracts of the lysimeter soil samples were partitioned between aqueous and organic phase to examine how much of the cinosulfuron applied to the lysimeter soils was transformed into polar metabolites, the ^{14}C-activity distributed into the aqueous phase was less than 10% of the total ^{14}C in the soil extracts in all samples (Table X). The fate of the [^{14}C]cinosulfuron applied to lysimeter soils is summarized in Table XI , where $^{14}CO_2$ evolved for 14 weeks from the soil surfaces in the first year and ^{14}C translocated in rice plants during the 2 years of cultivation were 2.0 ~ 3.6% and 3.2 ~ 4.1%, respectively, of the originally applied ^{14}C-activity, whereas most of the applied ^{14}C-activity (about 74.7 ~ 76.8% of the original ^{14}C applied) remained in lysimeter soils.

Table X. Distribution of ^{14}C-activity in the methanol extracts from the different layers of the lysimeter soil treated with [^{14}C]cinosulfuron and collected after harvest between aqueous phase and organic phase.
Aqueous phase + Organic phase = 100%

	Soil depth from the surface (cm)	Extracted with methanol[a] (%)	Distribution (%) of ^{14}C after partitioning[b]	
			Aqueous phase	Organic phase (CH_2Cl_2)
1st year	0 ~ 5	49.61	7.06	92.94
	5 ~ 10	33.53	10.02	89.98
2nd year	0 ~ 5	22.04	8.40	91.60
	5 ~ 10	29.33	7.11	92.89

[a] % the pre-extraction soil ^{14}C-activity
[b] The methanol extracts acidified down to pH 2

Table XI. Fate of [^{14}C]cinosulfuron treated onto rice plant-grown lysimeter soils during the experiment period. Radioactivity applied = 100%

	Lysimeter	$^{14}CO_2$[a] evolved	^{14}C volatile	^{14}C in rice plants	^{14}C leached	^{14}C remained in soil	Recovery (approx.)
		%					
1st year	I	2.03	BG[b]	2.42	BG	92.22	96.67
	II	3.58	BG	2.98	BG	89.26	95.82
1st year ~ 2nd year	I	2.03	BG	3.22	0.53	74.68	80.46
	II	3.58	BG	4.07	0.58	76.78	85.01

[a] ^{14}C mineralized and volatilized during the period of 14 weeks after application of [^{14}C]cinosulfuron

[b] Background

Discussion

It was reported that the sulfonylurea herbicides in soil mainly underwent chemical hydrolysis and microbial breakdown, but photolysis and volatilization were relatively unimportant factors *(3,8)*. Chemical hydrolysis especially is the major degradation route in acidic soils, and their degradation is greater in warm, moist, light-textured, and low pH soils, but the microbial breakdown predominates in alkaline soils *(8)*. Similarly, small amounts of $^{14}CO_2$ were evolved and no ^{14}C volatile substances were detected in our experiment. Very small amounts of [^{14}C]cinosulfuron equivalents were detected in the leachates collected from the lysimeters for 75 weeks, and after 2 years of rice cultivation, most of the ^{14}C applied onto the lysimeter soil surfaces was distributed in the 0 ~ 15 cm layer of the two lysimeters, indicating its low mobility in soil. Some researchers reported that mobility of sulfonylurea herbicides in soil increased with higher soil pH and lower organic matter *(8)*, and acidic pesticides were adsorbed in moderate amounts on organic matter and in relatively low amounts on clay minerals *(13)*. Considering the physico-chemical properties of the lysimeter soil, the low mobility of cinosulfuron in soil would be due to its weak acidic properties (pKa=4.72) and the relatively high amount of organic matter of the lysimeter topsoil. The ^{14}C-activity of the leachates and the soil extracts partitioned between aqueous and organic phase indicated that a considerable amount of polar degradation products was formed during the leaching period. The polar degradation products would form conjugates with soil constituents including organic matter, increasing the bound residues. Therefore, cinosulfuron is not expected to pose any groundwater contamination problem because of the characteristics of its very low application rates, relatively low toxicity, and low mobility in soil. Cinosulfuron is absorbed primarily by shoots and roots and then translocated to actively growing meristematic tissues *(14)*. In the present investigation, more ^{14}C-activity was distributed mainly in the straw, and the amounts of ^{14}C in it decreased remarkably in the second year. When the ^{14}C-activity translocated to brown rice grains was calculated as cinosulfuron equivalents, it was less than the maximum residue limits (MRL) of 0.1 ppm set by Japan, suggesting that it would be safe for human beings. After rice plant cultivation, the amounts of non-extractable ^{14}C bound residues, dehydrogenase activity, and the number of microbial colonies increased a little compared with those before growing rice plants. It was reported that various kinds of sugars, amino acids, and organic acids are accumulated in the rhizosphere of rice plants (15), and a higher activity of dehydrogenase was observed in the rhizosphere of corn than in root-free soil *(16)*. Also, it is known that the rhizosphere is a zone of intense microbiological activity due to its higher concentration of carbohydrates, amino acids, vitamins and other growth-promoting substances *(17)*. Other researchers *(12, 18)* reported that when rice plants were grown on soils aged for 3 and 6 months and treated separately with the herbicide [^{14}C]bentazon and the systemic insecticide [^{14}C]carbofuran, the amounts of non-extractable ^{14}C bound residues and ^{14}C distributed into the aqueous phase increased remarkably with rice plant cultivation for 42 days. Lee et al. *(9)* also reported that dehydrogenase activity and the number of microbial colonies in the lysimeter soil treated with [^{14}C]carbofuran increased a little in the case of rice plant cultivation compared to the non-planted. Based on these results, it could be suggested that the population of microorganisms and the dehydrogenase activity in soil increased with rice plant cultivation by rhizosphere effects and then microbial degradation of the herbicide was accelerated to form various non-extractable conjugates and/or bound residues.

Acknowledgments

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Chapter 5

Variability of Solute Transport in Field Lysimeters

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Solute transport at the field-scale is inherently influenced by the spatial variability of soil properties. Lysimeter studies in undisturbed soils are subject to same variability as that encountered in field soils. In this paper, we present an experiment to assess the variability of solute transport within lysimeters. Bromide was applied to a series of lysimeters of 61 and 122 cm depth containing undisturbed, homogeneous sandy soil, and leached with two different flow rates of 30 and 60 mm d^{-1} under non-steady state conditions. There was substantial variability among the bromide breakthrough curves in the 61-cm lysimeter for both flow rates and in the 122-cm lysimeter for the lower flow rate. The variation of solute transport decreased when the lysimeter depth and the flow rate were increased. All breakthrough curves showed a prolonged tailing, indicating that there was a stagnant water zone present in the soil.

Lysimeters are widely used to study fate and transport of chemicals in soils. In particular, undisturbed lysimeters offer an excellent framework for studying pesticide behavior in field soils (*1*, *2*). In 1990, the German pesticide regulatory agency, the Biologische Bundesanstalt für Land- und Forstwirtschaft (BBA), included lysimeter studies in the procedures required for assessing the leaching behavior of pesticides in soils (*3*). In the United States, even though not required by the U.S. Environmental Protection Agency, chemical companies submit results from lysimeter studies as supplemental data to support registration of pesticides (*4*).

The use of undisturbed lysimeters for regulatory purposes, however, may experience problems due to spatial variability of soil properties. Data obtained from one lysimeter may not be reproducible in another lysimeter. Considerable variability in the amount of chemicals leached from replicate lysimeters has been reported (*5*, *6*).

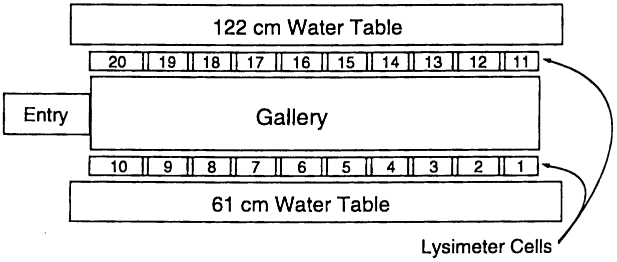
The aim of this paper is to evaluate the variability of solute transport in field lysimeters. Specifically, we compare the effects of flow rate and lysimeter depth on the variability of the breakthrough curve. Experiments with the conservative tracer bromide were carried out in a series of lysimeters containing undisturbed, homogeneous sandy soil. Bromide concentrations were measured in the drainage and the results analyzed with a numerical model.

Materials and Methods

Experimental Setup. Experiments were carried out at the lysimeter station of the University of Southern Florida in Tampa. The facility was specifically designed to study the capability of Florida soils to accept and treat septic tank effluents. Figures 1 and 2 show a plan view and a cross section of the facility, which was constructed in 1992. Twenty rectangular lysimeters are arranged along a central gallery. The surface area of the individual lysimeters is 61×184 cm^2. Most of the 24-m-long gallery is below grade, except for the top 76 cm of the roof. Gutters were installed along the exposed portion of the roof to prevent rainwater penetration. The walls of the gallery were covered with a plastic film. At both sides of the gallery, a 17 m long, 61 cm wide, and 61 cm deep trench was excavated, about 45 cm from the gallery wall. Each of these trenches was divided into eight cells, separated by 20.3 cm barrier walls, which prevented water movement from one cell to another. The trenches were filled with a 23-cm thick layer of coarse aggregates of size from 2 to 4 cm. On top of this layer, PVC pipes of 180-cm length and 2.5-cm i.d. were centered along the individual cells. The pipes contained holes of 1-cm i.d. spaced every 30 cm that provided influent distribution. The pipes were covered with an additional 7-cm-thick layer of aggregates, and the entire trench was covered with a geotextile fabric and backfilled with soil material (Figure 3). Two control cells containing only undisturbed soil were established at both ends of each trench.

Stainless steel pans were installed horizontally from the gallery at 61 cm and 162 cm below the undisturbed soil surface (Figure 2). Slots were cut from the gallery walls and the pans were forced into the slots with hydraulic jacks. The pans were 61×102 cm^2 in size and had a 5-cm lip on three sides. A crease at the center along the long axis provided a conduit for drainage water towards attached tubes that lead the drainage to collection flasks inside the gallery. In addition to the pans, the lysimeters were instrumented with porous ceramic solution samplers and tensiometers at regular depth intervals.

On the outside of each of the lysimeter strips, a trench of 23-m length and 1.83-cm width was excavated for the installation of artificial water tables. A wooden frame of 15-cm height was placed at the bottom of the trench and lined with a 10 mil polypropylene sheet, forming a water-impermeable basin. The basin was filled with a 2.5-cm sand layer followed by pea gravel. A perforated PVC pipe of 2.5-cm i.d. was installed horizontally along the entire length of the trench for water supply. The box frame was then covered with a geotextile fabric, and


122 cm Water Table
20
19
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Gallery
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1
61 cm Water Table
Lysimeter Cells

Figure 1. Plan view of the lysimeter facility at the University of Southern Florida.

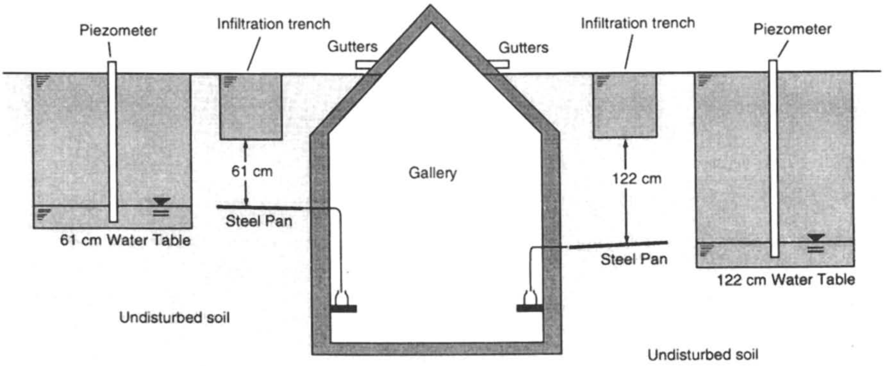
Piezometer
Infiltration trench
Gutters
Gutters
Infiltration trench
Piezometer
61 cm
Gallery
122 cm
Steel Pan
61 cm Water Table
Steel Pan
122 cm Water Table
Undisturbed soil
Undisturbed soil

Figure 2. Cross section of the lysimeter facility at the University of Southern Florida.

Table I. Experimental scenarios for the bromide tracer test.

Lysimeter	*Low Flow Rate*		*High Flow Rate*	
Depth	*Septic Tank Effluent*	*Water*	*Septic Tank Effluent*	*Water*
61 cm	2, 5, 8[a]	4	3, 6, 9	7
122 cm	13, 15, 17	19	12, 14, 18	16

[a] Numbers correspond to the lysimeter number shown in Figure 1.

the trench backfilled with native soil material. Three piezometers were installed along each trench for monitoring water table height. During operation of the lysimeter facility, an artificial water table in the lysimeter was maintained by supplying water to the impermeable basin and allowing continuous overflow to the adjacent soil.

Hydraulic Properties of Soil Material. Three test pits were excavated for determination of soil properties in the immediate neighborhood of the lysimeter facility. The soil was characterized as a Candler fine sand (Quartzipsamment). Particle size analysis indicated that the soil at the site was very uniform and consisted of 97 to 98% sand, 0.1 to 0.5% silt, and 1.5 to 3.1% clay. The bulk density of the material ranged from 1.46 to 1.54 kg L^{-1}. Saturated hydraulic conductivity and water retention characteristics were obtained from undisturbed soil cores. The saturated hydraulic conductivity determined by the constant head method ranged from 555 to 680 cm d^{-1}. The water retention characteristics showed little variability (Figure 4).

The hydraulic functions were parameterized with the Mualem-van Genuchten model (*7*). Figure 4 shows the best fit of the water retention function to all experimental data and the predicted unsaturated hydraulic conductivity relation. The hydraulic parameters were estimated with the RETC code (*8*), and the parameter values of the hydraulic functions are: $\theta_r = 0.05$ m^3m^{-3}, $\theta_s = 0.4$ m^3m^{-3}, $\alpha = 0.018$, and $n = 7.15$, where θ_r is the residual water content, θ_s is the saturated water content, and α and n are shape parameters. The analysis of the soil properties demonstrated that the soil at the lysimeter facility is very uniform in horizontal as well as in vertical direction.

Tracer Experiments. The lysimeters were operated under two different infiltration regimes: one with a low flow rate of 30 mm d^{-1}, the other with a high flow rate of 60 mm d^{-1}. The infiltration was applied in six doses per day, at 6 am, 7 am, 8 am, 12 am, 6 pm, and 7 pm. To study the capability of the soil to treat wastewater, some of the lysimeters were loaded with septic tank effluent. Table I shows an overview over the different experimental conditions.

The tracer test was started on February 24, 1996 at 4.30 pm. A bromide solution of 10 g Br^- L^{-1} was applied to each lysimeter as short pulse input. The tracer was then leached through the soil by the water/wastewater dosing described above and sporadic rainfall. Drainage outflow collected by the pans was analyzed for bromide with an ion selective electrode.

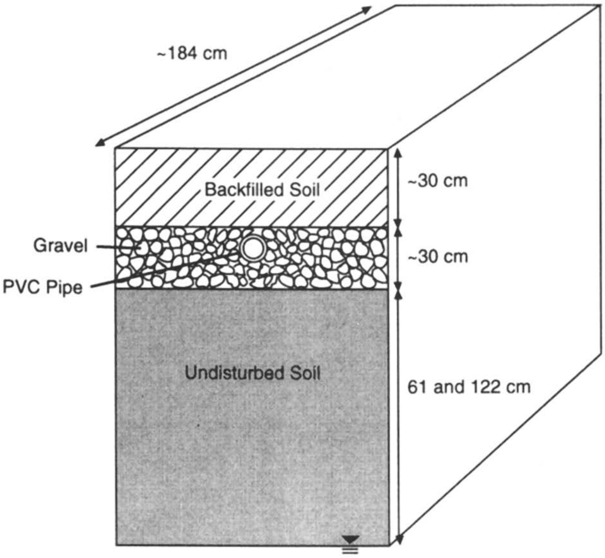
~184 cm
Backfilled Soil
~30 cm
Gravel
PVC Pipe
~30 cm
Undisturbed Soil
61 and 122 cm

Figure 3. Schematic view of a lysimeter and the infiltration system.

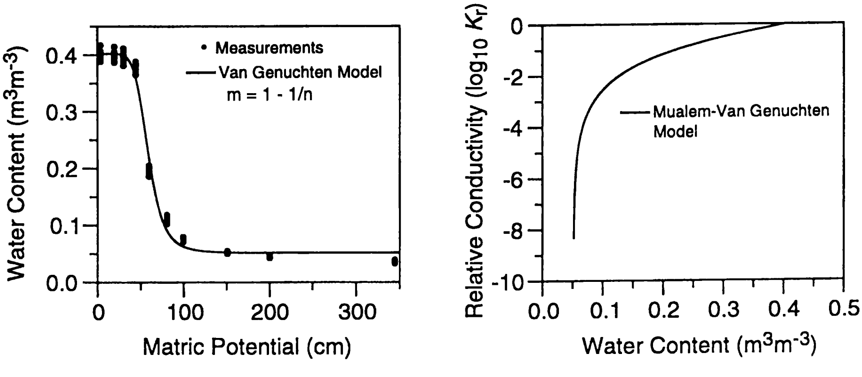

Figure 4. Measured water retention characteristics and hydraulic functions of lysimeter soil. Data points represent measurements from various depths in all three pits.

Modeling. The mathematical modeling is based on the following assumptions:

1. Water transport is described by the one-dimensional Richards' equation (*9*). The hydraulic functions are given by the Mualem-van Genuchten parametrization (*7*), as shown in Figure 4.
2. Transport of the conservative tracer bromide is described by the advection-dispersion equation (*9*). The hydrodynamic dispersion coefficient D is given as

$$\theta D = \lambda J_w \tag{1}$$

   where θ is the volumetric water content, λ is the dispersivity, and J_w is the water flux. For the fine sandy soil at the lysimeter site, a constant dispersivity of 0.5 cm is assumed (*10*).
3. The soil is initially void of the solute bromide. The initial conditions for the water flow problem are the equilibrium water contents and matric potentials for a stagnant water table at the bottom of the lysimeter.
4. A short pulse of bromide is applied to the lysimeters and leached with water. Water enters the lysimeter at the top by the artificial infiltration six times per day and by sporadic rainfall, as shown in Figure 5. The bottom of the lysimeter is water saturated and water exits by seepage. Solutes leave the system with the water drainage.

The governing equations together with the initial and boundary conditions as described above were solved numerically with the CHAIN_2D code (*11*). All model parameters, except for the dispersivity, were known from the experimental setup or independent measurements, such as the hydraulic properties. No parameter estimation or model calibration on the experimental bromide data has been performed.

Results and Discussion

Spatial Variability. Figure 5 shows the cumulative infiltration at the lysimeter surface for the 20 days of the experiment. Four rainfall events during the experimental period did not contribute substantially to the total amount of infiltration. The amount of rainfall was small compared to the artificial dosing. The jagged line for the cumulative infiltration is caused by the six daily dosing events.

The experimental bromide concentrations in the drainage water are depicted in Figure 6. There is no obvious difference between the septic tank effluent and the water infiltrations, and in the following discussion we therefore do not distinguish between these two types of treatments. For a given flow rate and lysimeter depth, there is considerable variability among the breakthrough curves, even though the soil was very homogeneous. It appears that there is less variability for the higher than for the lower flow rate. The data also indicate that the variability decreases when the lysimeter depth increases. The 122-cm lysimeter for the high flow rate showed most uniformity, except for the lysimeter Nr. 12.

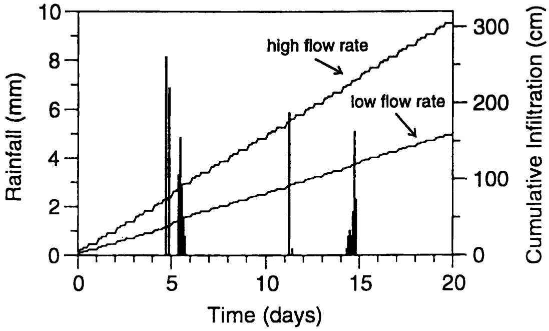

Figure 5. Rainfall and cumulative infiltration at the lysimeters.

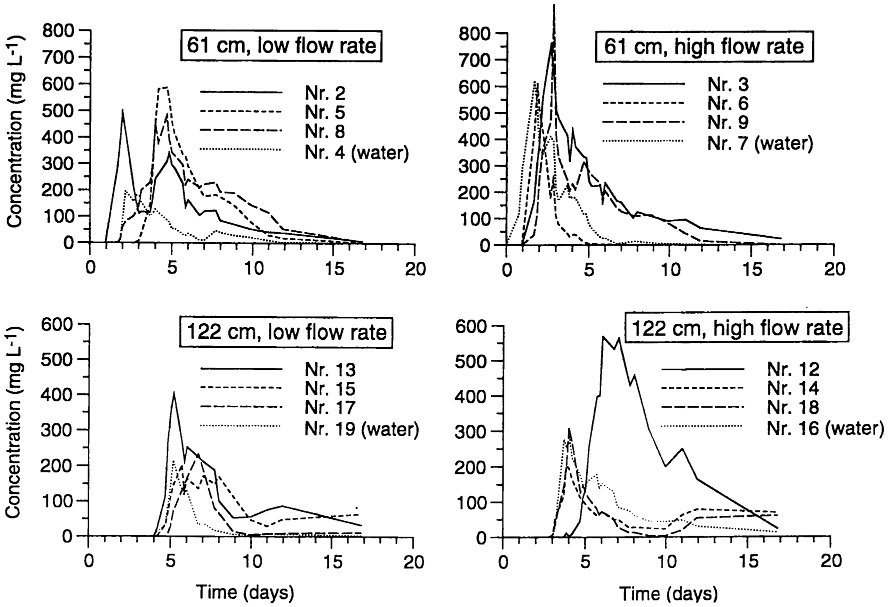

Figure 6. Experimental bromide breakthrough curves for different lysimeter depths and flow rates.

Despite the variability, most of the breakthrough curves have similar characteristics. The breakthrough curves are all skewed, with a steep initial increase followed by a prolonged tailing. In general, the curves show one dominant concentration peak, so that we can consider them as unimodal. As expected, solute breakthrough occurred earlier in the 61-cm than in the 122-cm lysimeters, and the higher flow rates resulted in faster mean solute transport. The skewed shape of our breakthrough curves are in agreement with results from Saxena et al. (*12*), who reported similar curves for chloride in a sandy soil under non-steady state flow conditions.

Modeling. The results of the modeling are illustrated in Figure 7. For better comparability, experimental data as well as model outputs were normalized. The jagged model curves are the result of the intermittent infiltration. As can be seen in Figure 7, the model breakthrough curves and also the experimental data are smoother for the 122-cm than for the 61-cm lysimeters. The longer travel distance dampens the infiltration pulsing.

The model calculations show two distinct features, consistent for all four cases. First, the model underestimates the experimental solute travel time. The experimental data show earlier occurrence of solute breakthrough and peak concentrations. Second, the model curves are rather symmetric and do not represent the prolonged tailing. Both observations indicate that there might be a physical nonequilibrium present in the lysimeters. Such a situation can occur if a portion of the water in the soil is stagnant and does not participate in transport. This conception is known as the mobile-immobile water model (*13*), and our results strongly suggest that this concept may be applicable to our experimental data. Our experimental results could also be caused by macropore flow. Saxena et al. (*12*) pointed out that even when the data do not show direct evidence of preferential flow, the latter might be present and cause unimodal breakthrough curves with tailing.

Effect of Increased Lysimeter Depth and Flow Rate on Solute Transport. When the lysimeter depth is increased, the solute travel time through the system becomes larger, and the variance of the travel time changes. The effects of increased lysimeter depth on solute transport can be somewhat compensated by increasing the flow rate. For saturated flow, the mean travel time $\mathrm{E}(t)$ through a lysimeter of depth L is given as

$$\mathrm{E}(t) = \frac{L\theta_s}{J_w} \tag{2}$$

where θ_s is the saturated volumetric water content. From Equation 2 it follows that when depth L and flow rate J_w are doubled simultaneously, the mean travel time of a solute remains unchanged. For unsaturated flow, however, this relationship is not true because the water content is not constant, and the mean travel times may be very different. This is illustrated in Figure 8, which shows simulated breakthrough curves for saturated and unsaturated conditions under

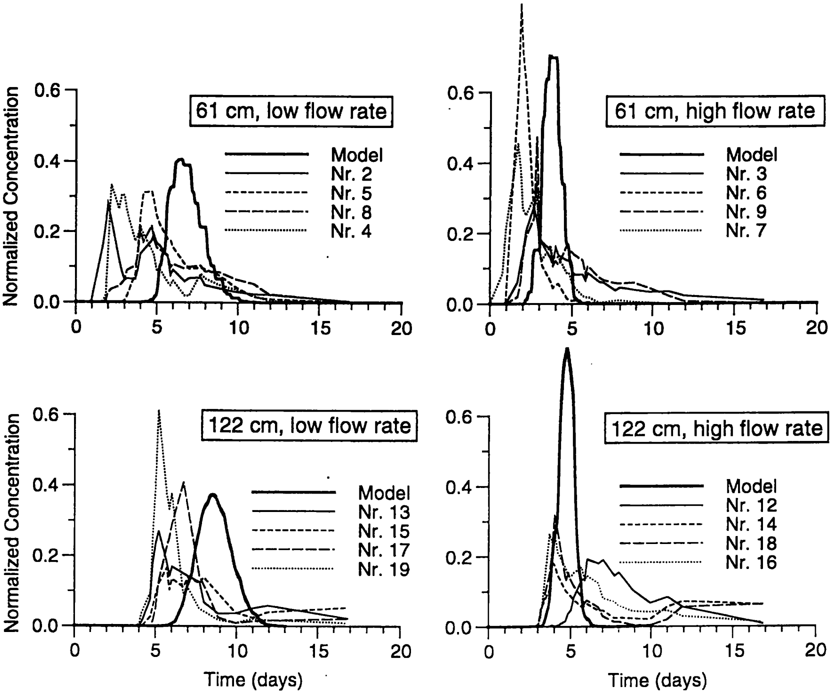

Figure 7. Normalized bromide concentrations and model simulations.

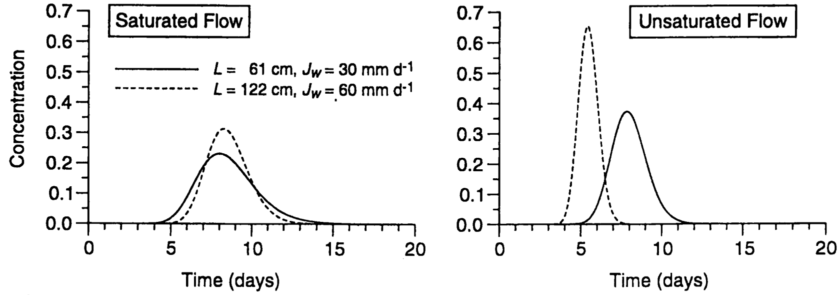

Figure 8. Theoretical breakthrough of a conservative tracer in the 61-cm and 122-cm deep lysimeters for steady-state flow rates of 30 mm d^{-1} and 60 mm d^{-1}.

otherwise identical steady-state flow rates. Note that for saturated flow, the two breakthrough curves are not identical, because the variance of the travel time is proportional to L/J_w^2 but not to L/J_w. Therefore the 61-cm lysimeter with the 30 mm d^{-1} flow rate shows a larger variance. For unsaturated flow, the mean travel times are very different, because the capillary fringe occupies a larger fraction of the total volume of the 61-cm lysimeter thereby increasing its average water content relative to the deeper lysimeter.

Conclusions

The experimental setup at the lysimeter facility at the University of Southern Florida allowed the assessment of the variability of solute transport in field lysimeters. Consistently, all measured breakthrough curves from the lysimeters were skewed with a prolonged tailing. This observation, together with the modeling results, indicate that there might have been a stagnant water zone within the soil, in compliance with mobile-immobile water or macropore flow concepts. Despite the very uniform soil at the experimental site, there was considerable variability of solute transport in the lysimeters. The variability decreased when either the flow rate or the lysimeter depth was increased. Considering the relatively high flow rates of 30 and 60 mm d^{-1} used in this study, we anticipate that under natural rainfall conditions the variability between the lysimeters would become more pronounced.

Acknowledgments

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Chapter 6

A Review of Herbicide Leaching Studies in Sweden: Field, Lysimeter, and Laboratory Measurements

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To characterize the mobility of pesticides in soil, results obtained in short-term laboratory tests are commonly used, along with data on degradation rates and physico/chemical properties of pesticides. However, the environmental conditions in such tests are quite different from natural field conditions in which biological, chemical, and physical processes occur in a complex soil structure, mostly under non-equilibrium conditions. Outdoor lysimeter experiments conducted under non-steady state flow conditions, are good alternatives to laboratory tests, which have demonstrated that they can simulate field situations quite well with respect to pesticide leaching. In this paper, results from a number of Swedish leaching studies with selected pesticides, carried out in monolith lysimeters, are described. Attention has been focused on comparing these leaching estimates with what one could expect in terms of mobility based on the inherent properties of the pesticides. Also, the impact of soil properties on pesticide leaching is discussed, as well as the importance of correctly evaluating the significance of measured concentrations and loads of pesticides obtained in lysimeter experiments in terms of actual field situations.

Transport of agricultural chemicals through soils has become a problem of international concern, due to its potential for causing deterioration in surface water and groundwater quality. Although the concentrations in these environments are usually very low and typically below levels of toxicological concern (*1*), a significant number of pesticides have been detected (e.g. *1,2,3*), which are often attributed to leaching through the unsaturated zone.

Along with the increasing concern about pesticide contamination of various water bodies, much emphasis has been put on designing suitable methods to characterize leachability in soil. In development of regulatory decision schemes, such considerations are extremely critical. This far, we have relied heavily on results obtained in short-term laboratory leaching tests, along with data on physico/chemical

In The Lysimeter Concept; Führ, F., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 1998.

properties of pesticides (*4*). However, such leaching tests are mostly performed in homogeneous, uniformly packed sand under saturated steady-state flow conditions and are therefore not typical of natural field situations. In contrast, outdoor lysimeter experiments, which are normally conducted with unsaturated soil over much longer periods, have demonstrated that they can simulate actual field conditions quite well with respect to leaching of pesticides in soil (*5*). The small size and therefore easiness to control water flows and environmental conditions in lysimeter experiments, contribute to make them very suitable for characterization of pesticide leaching (*6*). However, one should also be aware of the limitations of lysimeters, which may impact on the results. For example, in freely drained lysimeters, the zero-tension bottom boundary will result in formation of a water-saturated zone at the bottom of the soil profile. This may certainly modify the soil-water conditions throughout the profile, especially for shallow lysimeters. Cutting off the monolith from the underlying soil prevents upward migration of water from layers that would typically support the profile with water in a field situation. This will also to some extent affect soil moisture conditions inside a lysimeter, especially during the growing season when the evapotranspirational demand is high.

In addition to direct measurements, mathematical simulation models are now increasingly being used to predict pesticide transport in soil. Models provide a relatively inexpensive way of estimating likely leaching behavior for a variety of environmental conditions, which would not be feasible with costly field studies. Accordingly, several simulation models are now available for prediction of pesticide fate in soil (*7*), and they are also at an increasing rate being built into various regulatory assessment procedures. However, one limitation for extensive use, especially of detailed mechanistic models, is the difficulty in determining appropriate parameter values. Also, in line with what is mentioned above; can we really trust pesticide parameter values determined in the laboratory, that are used in models, and are appropriate response functions for temperature and moisture included in the models.

In the following presentation, we discuss some of the major reasons for the commonly poor resemblance between leaching estimates which are based on laboratory studies and those that are obtained in field experiments. Also, the importance of correctly evaluating the significance of measured concentrations and loads of pesticides in lysimeter leachate in terms of actual field conditions is discussed. The presentation is based on results obtained in a selection of pesticide leaching studies carried out in undisturbed field lysimeters in Sweden.

Materials and Methods

Experimental Setup. The results presented here are based on measurements performed in 0.3-m diameter and 1-m deep monoliths, which were collected using a coring technique described by Persson and Bergström (*8*). With this method a standard PVC sewer pipe is gently pressed into the soil by a steel cylinder, equipped with four cutting teeth, which rotates slowly around the pipe as it penetrates the soil. After collection, the soil cores were prepared for free drainage and transported to a lysimeter station in Uppsala, equipped for collection of leachate. A schematic representation of this type of lysimeter is shown in Figure 1.

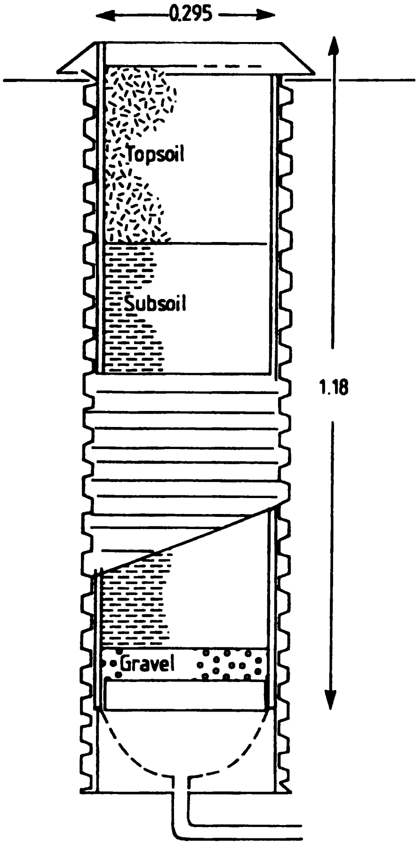
0.295
Topsoil
Subsoil
Gravel
1.18

Figure 1. Lysimeter placed in a below-ground pipe (dimensions in meters; adapted from *33*).

The active ingredients included in this overview are: bentazon chlorsulfuron, clopyralid, dichlorprop, fluroxypyr, metsulfuron methyl, and a non-registered molecule (Table I). Treatments included three soils ranging from loamy sand/sand to clay, different precipitation regimes resembling normal and worst-case conditions for Sweden, and normal and double the normal application rates of spring applied pesticides (Table II). Application of pesticides occurred in early June each year. All lysimeters were cropped with spring barley (*Hordeum distchum* L.), grown according to normal agricultural practices, i.e. sown in May and harvested in August/September.

Table I. Chemical Names of the Included Compounds

Common Name	*Chemical Name*
Bentazon	3-(1-methylethyl)-(1*H*)-2,1,3-benzothiadiazin-4(3*H*)-one 2,2-dioxide
Chlorsulfuron	2-chloro-*N*-[[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)amino] carbony]benzenesulfonamide
Clopyralid	3,6-dichloro-2-pyridinecarboxylic acid
Dichlorprop	(±)-2-(2,4-dichlorophenoxy)propanoic acid
Fluroxypyr	[(4-amino-3,5-dichloro-6-fluoro-2-pyridinyl)oxy]acetic acid
Metsulfuron methyl	2-[[[[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)amino] carbonyl]amino]sulfonyl]benzoic acid

Analytical Methods. The acidic compounds (dichlorprop, bentazon, clopyralid, fluroxypyr, and the non-registered molecule) were extracted with dichloromethane after acidification (*9*), except fluroxypyr, which was extracted with ethyl acetate before being transferred to dichloromethane. Quantitation of these compounds was by gas chromatography (*10*) with detection limits between 0.1 and 1 $\mu g\ L^{-1}$.

Chlorsulfuron and metsulfuron methyl were analyzed with ELISA (Enzyme-linked Immunosorbent Assay) Microplate Immunoassays (*11,12*), with detection limits of 0.0125 and 0.010 $\mu g\ L^{-1}$ for chlorsulfuron and metsulfuron methyl, respectively.

Results and Discussion

Pesticide Properties as Predictors for Pesticide Leaching. All the compounds included here are considered to be fairly mobile based on the information obtained in laboratory tests (Table III). However, when considering the amounts of the pesticides that actually leached out during periods from 7 to 11 months in the lysimeter studies, all seemed relatively non-leachable; i.e, <0.2 % leached out of the amounts applied, with exception of the non-registered molecule (Table III). For example, no detectable concentrations of clopyralid were found in leachate, despite a listed K_{oc}-value of 6 mL g^{-1}, a half-life of 40 days (*13*), and a water solubility of 1.0 g L^{-1} (*14*). Moreover, when comparing adsorption and degradation of bentazon and dichlorprop (Table III), both tested in the same soils, one would expect the former to

Table II. Soils, Experimental treatments and Selected Results of Some Swedish Lysimeter Studies

Herbicide	*Dose (g a.i. ha^{-1})*	*Soil Type*	*Prec. + Irr. (mm)*	*Leachate (mm)*	*Leached Mass (g a.i. ha^{-1})*
Chlorsulfuron	4/8	Loam[†]/sand[‡]	555[§]	154/158[§]	0.005/0.013[§]
Metsulfuron methyl	4/8	Loam/sand	447[¶]	86/87[¶]	0.000/0.005[¶]
Dichlorprop	1600	S.loam/sand	518/603[#]	79/142[#]	0.48/0.91[#]
	1600	Clay/clay	518/603[#]	158/196[#]	3.22/0.26[#]
Bentazon	600	S.loam/sand	583/619[§]	124/250[§]	0.00/0.10[§]
	600	Clay/clay	583/619[§]	268/280[§]	0.06/0.44[§]
Clopyralid	120/240	Loam/sand	609[§]	226/231[§]	0.00/0.00[§]
Fluroxypyr	188/375	Loam/sand	609[§]	221/237[§]	0.00/0.00[§]
Non-reg. molecule	900	S.loam/sand	583/619[§]	124/250[§]	1.26/5.82[§]
	900	Clay/clay	583/619[§]	268/280[§]	20.54/14.99[§]

[†] Topsoil classification; [‡] Subsoil classification; [§] 11-month period; [¶] 7-month period; [#] 9-month period.

Table III. Physico/chemical properties, degradation and leaching of some herbicides

Herbicide	*K_{oc} (mL g^{-1})*	*Half-life (days)*	*Water Solubility (g L^{-1})*	*Leached of Appl. (%)*
Chlorsulfuron	40 (pH 7)[†]	40[†]	27.9 (pH 7)[‡]	0.02-0.16[§]
Metsulfuron methyl	35 (pH 7)[†]	30[†]	2.79 (pH 7)[‡]	0.00-0.06[§]
Dichlorprop	20-25[¶]	1-4[#]	0.35[‡]	0.03-0.20[††]
Bentazon	34[†]	20[†]	0.5[‡]	0.00-0.07[††]
Clopyralid	6[†]	40[†]	1.0[‡]	0.00[‡‡]
Fluroxypyr	51-81[§§]	7-55[§§]	8.0[§§]	0.00[¶¶]
Non-reg. molecule	12-40[§§]	10-35[§§]	1.7[§§]	0.14-2.28

[†] Wauchope et al. (*13*); [‡] Tomlin (*14*); [§] Bergström (*27*); [¶] Ghorayshi and Bergström (*30*); [#] John Stenström (pers. comm.); [††] Bergström and Jarvis (*20*); [‡‡] Bergström et al. (*31*); [§§] Data from the manufacturer; [¶¶] Bergström et al. (*32*).

leach at larger amounts. However, this was shown not to be the case (Table III). Bentazon was also tested in the same monoliths as the non-registered molecule, which had listed properties identical to bentazon (Table III). Still, leaching of the former compound was about 33 times higher than for bentazon. These examples stress that there are several problems involved in classifying pesticide leaching based only on physico/chemical properties and degradation. The environmental fate of pesticides in natural soils is a reflection of many interacting processes occurring in a complex soil structure under non-steady state conditions, which makes extrapolation from the laboratory to field quite difficult. Assigning a single value on pesticide parameters determined in the laboratoty, such as half-life and sorption coefficients, ignoring all site specific differences with regard to soil, climate, etc, is very simplistic, since pesticide persistence and mobility are known to be affected by all of them.

In terms of degradation, field studies usually take several forms of dissipation into account (e.g. leaching, volatilization), whereas in most laboratory studies, losses only occur through degradation and thus overestimate the maximal residence time of a compound in soil. On the other hand, laboratory studies of degradation are usually carried out under constant optimal conditions with regard to temperature and moisture, which would likely favor degradation as compared with ambient field conditions. This was clearly demonstrated in the experiment in which leaching of dichlorprop was estimated. Detectable concentrations in leachate were found eight months after herbicide application, even though the persistence times in sandy topsoil samples in laboratory tests were as short as 2 days (*15*). Clearly, the degradation rates and mode of degradation determined under laboratory conditions (rapid, metabolic degradation) did not seem to occur under the field conditions which dichlorprop was exposed to in this study. Also, in a field situation, pesticides generally exhibit increasing persistence over time as more rapidly degraded fractions disappear, such as pesticide residues on the soil surface (*13*); this type of behavior is usually not captured in single half-life values determined in the laboratory.

Sorption/desorption constants are normally also determined at constant laboratory conditions, typically by shaking a slurry of soil in a $CaCl_2$ solution. In such a system the solvent is the continuous phase and the soil material is the dispersed phase with a seriously destroyed structure. However in the unsaturated zone of natural soils the solid material is the continuous phase with water distributed on surfaces and in pores. Consequently, sorption/desorption of pesticides in natural soils will be dependent not only on the rapid and reversible equilibria which are measured in laboratory studies using soil slurries, but also on slow non-equilibrium time-dependent transport of the componds on soil surfaces and in the soil pore space (*16*). In some cases, it has been shown that several weeks to years would be required to reach true sorption equilibrium (*17*), which is far beyond the time frames which we use in batch-equilibrium experiments.

In terms of temperatures under which sorption/desorption rates are determined, we typically use a value within the interval 20-25°C, although clear temperature dependence for this process has been noted (e.g. *18*). For example, in a study in which sorption of the herbicide linuron was determined at different temperatures in three soils (two sandy soils and one clay soil)(*19*), two of which were included in the leaching studies described here, some general patterns could be observed; i.e: i) when data were fitted to the Freundlich sorption isotherm function, the non-linearity of the sorption isotherms increased with decreasing temperature; ii) the sorption changed significantly with varying temperature in all soils; and iii) the temperature dependence in sorption was generally stronger at lower concentrations. In one of the sandy soils, K_{oc} was about three times higher at 5 °C than at 23°C, both in the topsoil (0-30 cm) and in the subsoil (30-60 cm). The implication of this pattern when extrapolating from laboratory to field as a basis for assessing leaching behavior is obvious, especially for colder regions and climates. In central Sweden, for example, only 5 months out of the year have long-term average air temperatures exceeding 10°C, and none that reaches 20°C. The temperature dependence of sorption/desorption of the herbicides included in this overview is, more or less, impossible to assess based on the measurements described here for a different compound. Still, there is reason to believe that such temperature effects contributed to the poor resemblance between what could be predicted from laboratory derived sorption estimates and field leaching data (Table III).

Another contributing factor to the deviations between laboratory and field based leaching assessments is that we tend to focus entirely on the topsoil when we determine pesticide properties in the laboratory. Leaching in the field involves the whole profile, which stresses the importance of investigating soil chemical/biological properties of importance for fate and mobility (e.g. sorption, degradation) also in deeper soil layers. The fact that biochemical processes are more prevalent in topsoil than in subsoil, mainly due to higher organic matter content in the topsoil, usually increases the persistence and therefore also the risk for leaching of the fraction of a compound that has moved into the subsoil (*20*).

Influence of Soil Properties on Pesticide Leaching. There are several studies showing that soil physical conditions may also have a major impact on pesticide leaching which confound compound related properties (e.g. *21,22,23*). In all the studies referred to in this summary, non-equilibrium flow processes related to soil structural features considerably influenced pesticide leaching. For example, peak concentrations of chlorsulfuron and metsulfuron methyl eluted after only 70 mm of accumulated leachate, which was clearly less than one pore vloume. A similar leaching pattern was observed for the other compounds. There was also large differences between the sandy soils and the clay soils with regard to leaching pattern. In the study with bentazon, more than four times as much of the compound leached from the clay soil than from the sandy soil (Table II). A similar situation was also applicable to the non-registered molecule, for which peak concentrations in leachate from the clay soil reached 19.3 $\mu g\ L^{-1}$ in the beginning of the drain-flow period in autumn (about 4 months after herbicide application), whereas maximum concentration in the sand was only 7.1 $\mu g\ L^{-1}$ in the following spring (Figure 2), with correspondingly larger leaching loads in the clay soil (Table II). These examples were taken as clear evidence of preferential flow.

Even though non-equilibrium flow in structured soils commonly increase pesticide leaching, as shown above, it may in some cases also reduce leaching. This will occur if the compound is mixed in with and protected in the soil matrix, and water is rapidly moving through soil without any interaction with the soil matrix (*24*). Also, accumulation of organic matter from root residues in root channels may contribute to increased biological degradation of pesticides, which will reduce leaching, even though root channels act as macropore-flow pathways. This was

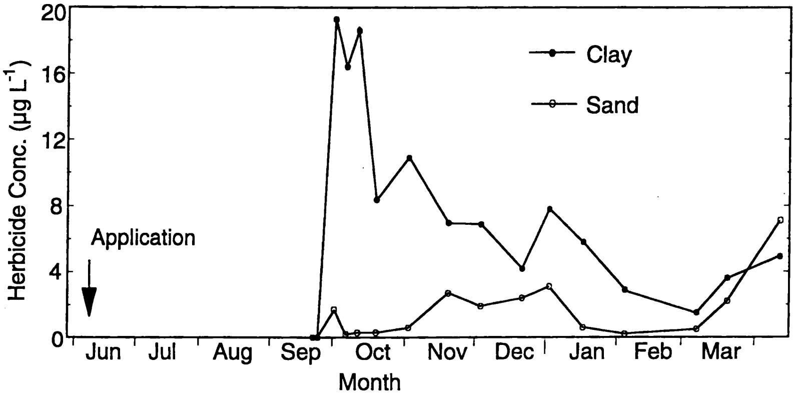

Figure 2. Concentrations of the non-registered herbicide in leachate from sand and clay monoliths.

clearly demonstrated by Gish et al. (*25*) in a study comparing the effects of tillage vs. no-tillage systems on pesticide leaching in deep well-drained soils. They observed that, although, atrazine initially moved deeper in the top 0.6 m of the soil profile in a no-tillage system, atrazine concentrations below 1.2 m depth were always lower than under tilled conditions. The reduction of atrazine leaching under no-tillage ralative to tilled systems was attributed to the accumulation of carbon and microbial biomass in the root channels. It is also quite common that, although, transient flow peaks shortly after pesticide application cause elevated concentrations in leachate from a clay soil, the pesticide loads over longer periods are quite small; often smaller than the corresponding loads from a sandy soil (*15*). Nevertheless, whether preferential flow will increase or decrease pesticide leaching over the long-term, it is certainly a factor that will ultimately contribute to poor resemblance between laboratory and field estimates of pesticide dissipation.

A potential problem with lysimeters is that water and water-carried chemicals may flow along the inside lysimeter wall, thereby affecting pesticide leaching in the same way as macropore flow. The extent of this problem for the type of lysimeter used here was assessed in an experiment in which clay and sand monoliths were treated with two non-reactive tracers, ^{36}Cl and tritiated water (*15*). Each tracer was applied on equally large areas, one in the center half and the other in the outer half of the monolith surface. In both soils, the tracers appeared simultaneously in leachate; although, quite different in the sand compared with the clay. In the sand, 100 mm of leachate had accumulated before the tracers eluted, whereas in the clay relatively high concentrations were recorded after only a few millimeters of leachate had been collected. The latter observation is clearly indicative of macropore flow in the structured clay. Also, the results showed that side-wall flow is not a problem for this type of lysimeter, when exposed to non-steady state flow conditions.

Interpretaion of Leaching Estimates Obtained in Lysimeters. The pesticide concentrations measured in lysimeter leachate are typical of the levels reached in soil water leaving the root zone in a field setting. If we wish to convert these concentrations to surface water and groundwater loadings in a given watershed, several factors have to be considered. In the field, the hydrogeologic conditions, which determine the net vertical pressure gradient in the groundwater flow, will ultimately set the boundaries for potential groundwater contamination and surface water contamination. These conditions vary considerably in the landscape, and it is therefore difficult to specify standard values for the ratio between shallow subsurface flow and groundwater percolation. Still, it is important to keep them in mind when interpreting the lysimeter data for real world scenarios. Water reaching the soil surface as precipitation may at times form surface runoff (i.e. when rainfall intensity exceeds the infiltration rate), which is normally not considered in lysimeter studies, even though it may occur (*26*). Another factor requiring consideration when converting lysimeter results to large-scale field conditions is land-use pattern as it relates to different hydrologeologic conditions. For example, it is important to note the portion of a watershed that serves as the recharge area to a groundwater reservoir and was treated with the pesticide of concern. Also, degradation of the pesticide in water and possible carry over of residues from previous years should be taken into account.

In a risk assessment for potential surface water pollution, based on the lysimeter study with chlorsulfuron and metsulfuron methyl, it was estimated that the measured peak concentrations of ca. 0.02 µg L^{-1} in leachate and the corresponding loads (Table II) were lowered about one order of magnitude if converted to reflect river water concentrations (*27*). These estimates were based on the 'diluting' factors mentioned above.

A factor of importance when interpreting pesticide leaching loads estimated in lysimeters in terms of actual field conditions, is the significance of the analytical detection limit. For example, the difference in leaching estimates of bentazon and dichlorprop, which were studied in parallel, was much larger than listed in Table II, that is, if we consider the five times higher detection limit for dichlorprop (0.5 and 0.1 µg L^{-1} for dichlorprop and bentazon, respectively). Only two water samples had bentazon concentrations over 0.5 µg L^{-1}. Similarly, the fact that leaching loads of fluroxypyr were zero (Table II), could merely be attributed to the relatively high detection limit of this compound (1.0 µg L^{-1}). On the other hand, if we had considered that the analytical detection limit of bentazon in fact was lowered from 0.1 to 0.05 µg L^{-1} for most of the water samples collected later in the season (which was not considered in the estimates listed in Table II), considerably larger leaching loads would have been estimated for this compound. Indeed, this would result in an increase from 0.06 to 0.14 g a.i. ha^{-1} for one of the bentazon treatments. These few examples demonstrate the importance of correctly evaluating the significance of calculated leaching loads of pesticides, especially when the concentration levels are close to the limit of quantification, which is often the case.

An interesting observation related to the above discussion on analytical detection limits and interpretation of results, is when we compare measured leaching loads and those obtained from model simulations. For example, when 4 g a.i. ha^{-1} of chlorsulfuron was applied, 0.005 g a.i. ha^{-1} was observed to leach during the 11-month period (Table I). In a model simulation using the MACRO model (*28*), the corresponding predicted leaching load was doubled (0.010 g a.i. ha^{-1}), even though the measured and predicted leachate volumes and concentration peaks were similar (*29*). The simple reason is that predictions include loads calculated from leachate volumes and pesticide concentrations below the detection limit, whereas concentrations below the detection limit were set to zero when determining the measured masses leached. In other words, it is not relevant to compare predicted and measured leaching loads when concentrations are close to the detection limit. This, as well as the implications of changing detection limits discussed above, is very critical in the context of regulatory authorities introducing criteria for acceptable leaching losses, as is currently being discussed around the world.

Conclusions

Results from the leaching studies presented in this overview suggest that we need to be precautious when using laboratory data on pesticide properties for assessment of possible petsicide leaching in the field. Accordingly, laboratory data may not always be a reliable source of input data to pesticide leaching models which attempt to describe field conditions. Indeed, environmental risk assessments for pesticide dissipation and mobility should mainly be based on results from field studies. Still, results obtained in laboratory studies, such as estimates of persistence and sorption/desorption are appropriate as preliminary indicators to suggest when further field tests are needed. One possible way to carry out a comprehensive, but relatively inexpensive field leaching test is to use monolith lysimeters, which offer an excellent experimental framework for studies of pesticide leaching. The value of lysimeters is that they not only allow the investigator to control all water movements through the soil but also allow manipulation of environmental factors as well.

There are also various soil properties that have a considerable impact on pesticide leaching which confound pesticide related properties, of which preferential-flow processes have proven to be among the most important ones. In this overview, it was shown that leaching of pesticides in clay soils may be as large or even larger than in sandy soils, due to the occurrence of macropore flow in the former. Therefore, we cannot safely assume that measurements of leaching in sandy soils always represent worst-case conditions, even though the water-holding capacity in sandy soils is much smaller than in clay soils.

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Chapter 7

Mobility and Degradation of Pesticides and Their Degradates in Intact Soil Columns

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Laboratory studies were conducted to determine the mobility of parent pesticides and degradation products through the use of large undisturbed soil columns. The influence of vegetation on the mobility of pesticide adjuvants was also investigated. Modifications to the laboratory setup of soil columns for studying various pesticides, degradation products, and adjuvants were done to fit the needs of the particular compound being studied. To improve mass balances of volatile parent compounds, such as methyl bromide, as well as biodegradable (mineralizable) pesticide degradation products such as deethylatrazine, modifications of columns to accommodate isolation of volatile degradation products were accomplished by enclosure of the column head space and use of flow-through systems. Evidence of preferential flow of atrazine, deethylatrazine, metolachlor, and methyl bromide were indicated by the presence of either the ^{14}C-compound or Br- (in the case of methyl bromide-applied soil columns) after the first leaching event. Diffusion through the soil matrix was also evident with a peak of ^{14}C in the leachate several weeks after pesticide (or degradate) application to the soil column. Deethylatrazine, a major degradate of atrazine, was more mobile than the parent compound. Vegetation had a significant positive effect on reducing the mobility of the adjuvants propylene glycol and ethylene glycol.

The fate of any pesticide in the environment is important to understand because of any potential detrimental effect; thus the environmental chemistry and environmental toxicology of a pesticide are inextricably linked. Similarly, the environmental fate of a pesticide encompasses both the movement and transformation of the compound. There is an interdependent linkage between these two processes: (1) the transformation products have mobilities that differ from the parent molecule, and (2) conversely, the mobility of a compound can have great impact on the transformation processes since the location of a molecule influences the types and rates of transformations that occur.

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Depending on their structure and physicochemical properties, soil-applied pesticides can move through runoff, leaching, volatilization, uptake into plants or microbes, or adsorption to the soil matrix. The conditions at each site are different, and the various agents that act upon the pesticide molecule can effect different types of transformations. The transformation products are typically degradates, although occasionally other types of transformations occur, such as conjugations, rearrangements, dimerizations, or isomerizations. The toxicological significance of any transformation product obviously needs to be considered for each compound. Recently there has been a realization that pesticide degradates are sometimes as important or more important than the parent pesticide in environmental settings. Although only a small minority of transformation products are of toxicological significance, serious consideration must be given to their formation mechanisms, quantities present, persistence, and mobility in the environment.

Investigations that focus on soil incubations, plant metabolism, or other component-based experiments have several distinct advantages, such as closely controlled environmental variables, low space requirements, and low cost per experimental unit which allows for more treatments and more replication. On the other hand, there are several shortcomings of very specific laboratory experiments, especially the lack of realistic environmental conditions variability and the scale. Research on larger scales, including field plots, fields, watersheds, or regions allows ample realism in conditions, variability, and scale, but such research has obvious limitations in investigators' capacity to control the variables such as climate; also, the costs of research are much higher at the larger scales.

Lysimeter research, as presented in this volume, represents a concept that optimizes the process of evaluating the environmental fate of pesticides. It incorporates many of the advantages of the laboratory approach, but retains essential elements of the realistic conditions encountered in the field. The scale is midway between the lab and the field, allowing for adequate replication, excellent sensitivity through the use of radiotracers, and manageable costs, but it also takes advantage of an intact soil monolith and natural weather conditions.

Utilization of intact soil columns for studying environmental fate of pesticides has some of the same advantages as the lysimeter concept. These are field-collected but studied under laboratory conditions. There are, of course, trade-offs once again, but they have one important advantage in common with the lysimeters. They provide an *integrated evaluation* of a compound's persistence, binding, degradation, and mobility in one experimental unit.

Laboratory mobility studies are often carried out using soil columns that have been created by packing sieved soils from various soil profiles into a PVC pipe or other cylindrical container. Pesticides applied at the surface move through the column with simulated rainfall. Pesticides or degradation products that are able to move by diffusion through the soil matrix along with water are retrieved at the bottom of the column. Concentrations are often measured by either gas chromatography (GC) or radiotracer techniques. The use of packed soil columns does not take into consideration the natural formation of macropores such as those created by plant roots or earthworm channels, and, thus, the contribution of preferential flow from rapid movement of the pesticides through such channels can not be determined. Czapar et al. (1) compared mobilities of alachlor, cyanazine, and pendimethalin in soil columns with and without artificial macropores. These herbicides were detected in leachates from only those columns with continuous macropores, and they state that leaching studies that use packed soil columns may underestimate herbicide mobility. With the use of undisturbed soil columns in laboratory studies, one can obtain a more realistic understanding of parent pesticide and degradation product mobility under less variable conditions than in the field. Maintaining the integrity of naturally occurring macropores allows for not only measurement of the mobility of compounds due to diffusion through the soil matrix, but also mobility due to preferential flow of compounds with water.

Methods for acquiring and setting up large undisturbed soil columns for studies conducted in this laboratory were modified from (2), who had used such methods to investigate solute transport through macropores in large undisturbed soil columns. The earliest studies in our laboratory using this method were conducted to determined the mobility of atrazine and major degradation products (3). In earlier fate studies of atrazine, volatility and evolution of CO_2 from its degradation were reported to be minimal (4,5), thus completely enclosing the headspace of the columns for this study was not necessary.

For a deethylatrazine mobility study (6), the soil column set up was modified to enable trapping of $^{14}CO_2$ in order to improve the mass balance of ^{14}C-deethylatrazine applied to the column. Evolution of the modification of the soil column continued with the study of metolachlor mobility (7). A preliminary study indicated a poor mass balance, and, thus, modification to make the system completely enclosed was carried out. A flow-through system was incorporated into the study so that the column was never opened to the atmosphere. Aerobicity was maintained, however, through a port that contained a charcoal trap to allow for air exchange while trapping organic ^{14}C that was generated from metolachlor degradation. In the mobility study of highly volatile methyl bromide (8), additional modifications to soil columns were undertaken. Instead of adding another separate section to the top of the soil column, a continuous PVC pipe was used, thus eliminating the seam between the column and the head space. Additionally, a charcoal trap was suspended in the column to trap methyl bromide that volatilized above the soil.

The influence of vegetation on the mobility of pesticide adjuvants was also investigated. For these studies, undisturbed soil columns were either seeded with alfalfa or rye grass or left unvegetated. During the establishment of vegetation, soil columns were maintained under controlled temperature and lighting conditions for 4 months, with water added to the columns as needed. After sufficient growth of plants had been achieved, as noted by the observation of roots at the bottom of the columns, adjuvants were applied to the soil, and a leaching study was begun.

Fate Studies in Intact Soil Columns

Mobility and Degradation of Atrazine. The fate of atrazine was determined in a laboratory study using large undisturbed soil columns taken from a field with no previous pesticide history (3). Intact soil columns were obtained from a field with no previous pesticide history at the Iowa State University Agronomy and Agricultural Engineering Farm, Till Hydrology Site, near Ames, IA. In order to obtain the undisturbed soil columns, a circular trench 70 cm deep was dug by using shovels, leaving a soil pedestal of approximately 40 cm in diameter in the middle of the trench. A furnace pipe measuring 15 cm in diameter and 60 cm tall was pressed gently into the top 2 to 3 cm of the soil pedestal, and soil was carved away at a depth of 5 to 10 cm in the same diameter as the furnace pipe before pushing the pipe further into the soil. In this way, compaction was avoided within the soil column. Physical and chemical characteristics of soils throughout the profile were determined (A & L Midwest Laboratory, Omaha) on subsamples of soils taken during column extraction.

Laboratory Preparation. In the laboratory, soil columns were prepared for laboratory experiments (Figure 1A). A polyvinyl chloride (PVC) pipe, measuring 20 cm in diameter and 60 cm in length, was centered around the soil column and the space was filled with molten parafin wax to prevent boundary flow along the outer edges of the columns during the leaching study (9). Prior to this step, the vertical surfaces of the soil columns were sealed with Plasti-Dip® spray (P.D.I., Inc., Circle Pines, MN) to prevent parafin from penetrating the soil column. An aluminum collar (15 cm tall) was fixed around the top of the soil column to prevent leachate from spreading over the wax during the leaching study. Once the wax was cooled and hardened, the bottom 1 cm of soil was removed, and a wire screen was placed in contact with the bottom of the soil column. A perforated Plexiglas™ plate (20-cm diameter) with six metal washers glued to it was mounted on the bottom of the PVC pipe. The washers served as spacers between the screen and the plate to prevent air locks and to assure continuous flow of leachate during the leaching study.

In order for the soil moisture of replicate columns to be equivalent at the beginning of the study, columns were saturated with 0.005 M $CaSO_4$ (2). This solution was chosen for soil saturation as its characteristics more closely resemble those of soil pore water than would ultrapure water. Each column was placed in a large metal garbage can, and $CaSO_4$ solution was added until columns were completely submerged. This submersion was done at a slow rate so that no air would be trapped within the soil column, with complete saturation accomplished over a 48-h period. Soil columns were then mounted in stands in a temperature-controlled room held at 25 °C and allowed to drain to field capacity. Ultrapure water was added to the top of each soil column and was then collected at the bottom to obtain a background leachate sample. A chloride tracer was applied to the top of the soil columns, which were then leached with ultrapure water to verify their performance (9). A qualitative comparison of the precipitate, arising from the drop-wise addition of 1 M $AgNO_4$ to the leachate, was made with background samples to ensure that the amount of chloride in the leachate was above the background level found normally in soil.

Soil Treatment. A solution was prepared with a mixture of Aatrex Nine-0® and [U-ring-^{14}C]ATR (98.2% radiopurity; Novartis Crop Protection, Greensboro, NC) dissolved in deionized water. Each column was applied with ATR at a soil concentration of 2.24 kg (active ingredient) per hectare and radioactivity level of 15 µCi of ^{14}C. The atrazine treatment was incorporated into the top 2 cm of soil. To minimize evaporation, the top of each soil column was covered loosely with aluminum foil. No attempt was made to trap for CO_2, since a previous soil metabolism study in this laboratory indicated minimal mineralization of ATR (< 1%) in soil the same field plot (4).

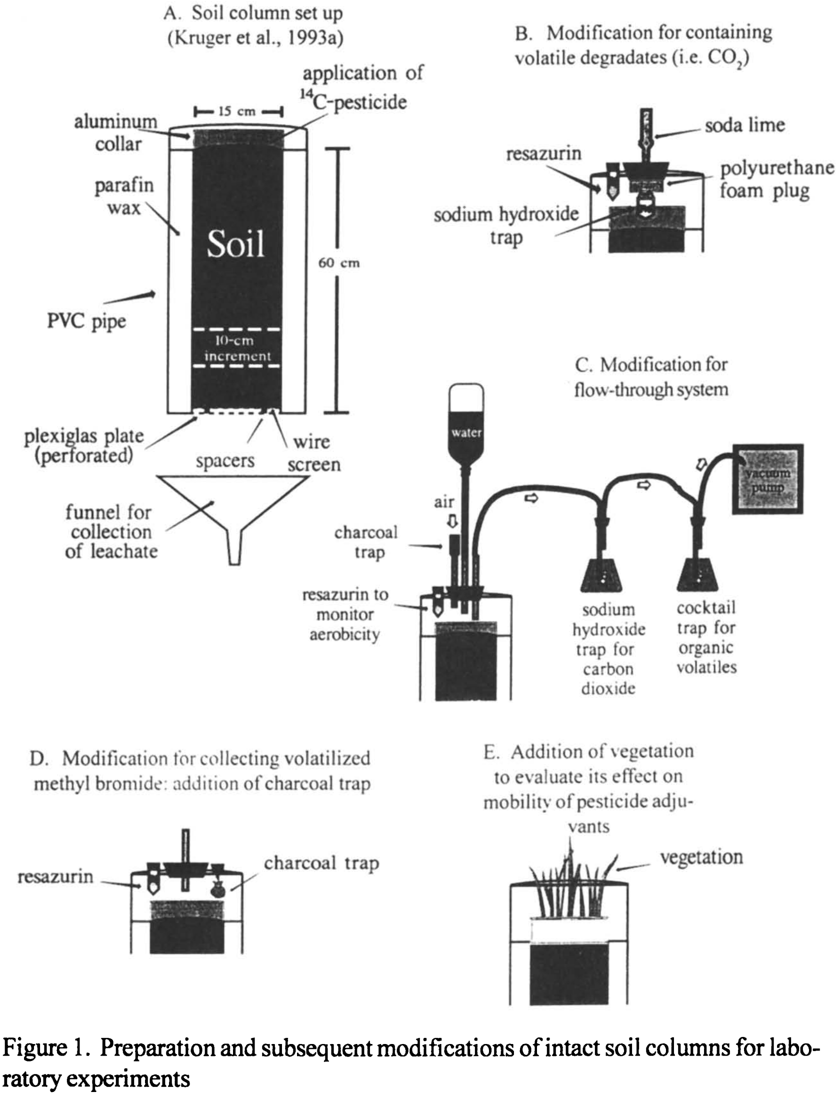
A. Soil column set up
(Kruger et al., 1993a)
application of
^{14}C-pesticide
15 cm
aluminum
collar
parafin
wax
Soil
60 cm
PVC pipe
10-cm
increment
plexiglas plate
(perforated)
spacers
wire
screen
funnel for
collection
of leachate
B. Modification for containing
volatile degradates (i.e. CO_2)
soda lime
resazurin
polyurethane
foam plug
sodium hydroxide
trap
C. Modification for
flow-through system
water
air
charcoal
trap
resazurin to
monitor
aerobicity
vacuum
pump
sodium
hydroxide
trap for
carbon
dioxide
cocktail
trap for
organic
volatiles
D. Modification for collecting volatilized
methyl bromide: addition of charcoal trap
resazurin
charcoal trap
E. Addition of vegetation
to evaluate its effect on
mobility of pesticide adju-
vants
vegetation

Figure 1. Preparation and subsequent modifications of intact soil columns for laboratory experiments

Leaching Study. So that mobility of not only the parent compound but also degradation products could be determined, a leaching study was not begun until three weeks after ATR treatment to allow for degradate formation from ATR. Soil columns were then leached weekly for 12 weeks with 3.8 cm of simulated rain (a quantity chosen to represent comparable rainfall amounts received during the spring in Iowa). The quantity of radioactivity recovered in leachate each week was determined by radioassaying subsamples of leachate by using liquid scintillation techniques.

Soil Extractions and Analyses. Following the leaching study, soil columns were cut into 10-cm increments. Subsamples from each depth (50-g dry weight) were extracted three times with 150 ml methanol/water (9:1), with an extraction efficiency for ATR of 100%. The extract was partitioned with dichloromethane, and subsamples of the concentrated organic fraction were radioassayed and used for thin-layer chromatography and autoradiography to determine the proportions of ATR and degradates. To determine the quantities of unextractable ^{14}C-residues, subsamples of extracted soils were combusted in a Packard sample oxidizer (Packard Instrument Co.).

Mobility and Degradation of Atrazine. In the leaching study, radioactivity was recovered in the leachate with the first rain event, indicating preferential (macropore) flow. Each week, approximately 0.1% of the applied radioactivity was detected in the leachate and, cumulatively, at the end of the 12-week period, 1.2% of the applied ^{14}C-ATR was recovered. With such a low amount of ^{14}C recovered in the leachate, no attempt was made to characterize the radioactivity (parent versus degradation products). Based on the proportion of ^{14}C to active ingredient in the treating solution, the cumulative concentration of ATR in the leachate was 7.6 µg/L.

The majority of the radioactivity remained in the top 10 cm of soil (77% of the applied ^{14}C), with the greatest proportion of ^{14}C as soil-bound (unextractable) residues (57%) (Figure 2). Deethylatrazine (DEA) was the most predominant degradate, with 3.6% of the applied ^{14}C characterized as DEA in the top 10 cm of soil. Deisopropylatrazine (DIA) was the second most predominant identified degradate. Polar degradation products (from the aqueous fraction after partitioning of the soil extracts) were greater in the top 10 cm of soil than in other depths.

In this study, ATR, along with the two degradation products DEA and DIA, exhibited the greatest mobility as they were detected at all depths. Their presence in soils of all depths of the column might also be attributed to degradation of ATR after reaching these depths.

Mobility and Degradation of Deethylatrazine. A study was conducted to determine the fate of deethylatrazine (DEA), a major metabolite of ATR, in large undisturbed soil columns (6). Soil columns (15-cm diameter x 60-cm length) were obtained from a field with no previous ATR history, as described in the ATR section. Two soil columns were prepared for laboratory experiments by using a modification of the method described by (3) (Figure 1B). In order to obtain a mass balance of the applied ^{14}C, the top of the column was sealed with an additional section of PVC pipe (20-cm diameter by 20-cm length), and the top of this section was capped with a plexiglas plate and sealed with silicon rubber adhesive sealant (General Electric Co., Waterford, NY) (6). Within the Plexiglas™ plate, three holes were cut. A large central hole, or port, was sealed with a neoprene stopper and used to access the top of the soil column during the leaching experiment. The stopper had a glass rod through the center which served as an attachment site for a polyurethane foam trap for trapping ^{14}C-organic volatiles. In order to trap $^{14}CO_2$ arising from complete mineralization of ^{14}C-DEA, a sodium hydroxide (NaOH) trap was suspended from a neoprene stopper in a second port. In order to assure that aerobic conditions were maintained, a perforated plastic centrifuge tube (capped with a neoprene stopper) containing 5 ml ultrapure water and two drops of a 4% resazurin solution was inserted to serve as a monitor for the aerobicity of the headspace over the soil column. All neoprene stoppers were wrapped with Teflon® tape.

Soil Treatment and Leaching. Each column received an application of DEA equivalent to 0.5 lb a.i./acre and approximately 20 µCi of [^{14}C]DEA by applying a treating solution prepared with a mixture of analytical grade DEA and [U-ring-^{14}C]DEA (94.8% radiopurity) [^{14}C]DEA dissolved in ultrapure water. The DEA treatment was incorporated into the top 2 cm of soil to minimize volatilization of DEA. Three days after treatment, a leaching study was initiated with an equivalent of 3.8 cm of rainfall (675 ml ultrapure water) applied slowly to the top of each column per week for 13 weeks. Rainfall applications usually took between 40 and 60 min. Leachate from each rain event was collected at the bottom of columns in 100-ml aliquots which were analyzed for radioactivity by liquid scintillation counting techniques (LSC).

Solid-phase Extraction (SPE) of Leachate. A modified SPE method was used to isolate DEA and degradates from the leachate (10). After filtering the leachates through a glass-microfiber filter, the pH was adjusted within the range of 7.0 to 7.5 by drop-wise addition of aqueous ammonia or phosphoric acid. For this procedure, Bond Elut® (Varian, Harbor City, CA) cyclohexyl SPE cartridges were used. After conditioning the cartridges with methanol and ultrapure water, leachates were passed through the SPE cartridges at a rate of approximately 5 ml/min, and then the cartridges were air-dried. DEA and degradates were eluted from the cartridges with 10 ml of acetonitrile. Effluent volumes were taken, and subsamples of the effluent and eluate were counted by using liquid scintillation spectroscopy, with radioactivity in the effluent categorized as unidentified polar degradates. DEA and degradates in the acetonitrile eluate were characterized by thin-layer chromatography on normal phase silica gel plates in a solvent system of chloroform: methanol: formic acid: water (100:20:4:2) (Novartis Crop Protection). Autoradiography was used to visualize the radioactive spots associated with ^{14}C-standards. TLC plates were scraped and counted using LSC techniques.

Soil Extractions and Analyses. At the conclusion of the leaching experiment, soil columns were cut into 10-cm increments, and subsamples were extracted and analyzed as described in the ATR section and in (3).

Statistical Analysis. For components of the leachate, an analysis of variance (ANOVA) was performed on the repeated measures design. Orthogonal contrasts were also determined for specific comparisons of leaching events. To determine the effect of soil depth, an ANOVA which used soil columns as a blocking variable was conducted on the components determined in soil extractions and analyses.

Mass Balance of DEA in Leachate and Soil. For this experiment, the overall mean recovery of radioactivity was 97%, with 89% of the applied radioactivity distributed throughout soil columns at the end of the leaching study. Less than 0.2% of the applied ^{14}C was recovered as $^{14}CO_2$, and no ^{14}C-organic volatiles were detected.

Preferential flow was noted during the first leaching event, with a significantly greater percentage of ^{14}C being leached in this rain event (2.3% of the applied ^{14}C) compared with all other rain events ($p = 0.0002$) (Figure 3). Of this amount, 1.3% was a characterized as DEA. There were no significant differences in the quantities of DEA leached from the columns for rain events 2 through 13. Unidentified polar degradates made up 1% of the radioactivity from the first rain event. After the sixth rain event, the concentration of polar degradates exceeded that of DEA in the leachate. Trace amounts (< 0.01%) of didealkylatrazine (DDA) and deethylhydroxyatrazine (DEHYA) occurred in the leachate throughout the leaching study. With the eleventh rain event, significantly greater DDA and DEHYA concentrations were noted, compared with all of the other rain events ($p = 0.002$ and $p = 0.004$, respectively).

Cumulatively, 7.5% of the radioactivity applied to the top of soil columns was recovered in the leachate over the course of the 13-wk leaching experiment. In consideration of the unlabeled analytical grade DEA associated with this quantity of radioactivity in the treating solution and taking into account the total volume of the leachate, this corresponds to a total DEA/degradate concentration of 10 μg/L (in DEA equivalents). With 3.6% as DEA, this corresponds to a concentration of 4.9 mg/L. The percentages of DDA and DEHYA in the leachate over the 13-wk study were less than 0.02% of the applied, while unidentified polar degradates accounted for 3.8% of the applied radioactivity. The unidentified polar degradates may have included DDA and DEHYA since the SPE method used may not have been as efficient for polar degradates including DDA and DEHYA, although it was efficient for isolating DEA. Recent research by (11) has focused on methods for isolation of polar degradates. In comparing the ATR-applied and DEA-applied soil column studies, it was noted that DEA was more mobile than ATR. After 12 weeks, 6% of the applied DEA was leached (DEA and degradates), compared with only 1% in ATR-applied soil columns (Figure 4).

Distribution of ^{14}C-DEA and Degradates in the Soil Profile. The top 10 cm of soil columns retained the majority of the applied ^{14}C (67%). The percentage of DEA was significantly greater in this depth (5.5%) than in the remaining depths ($\leq$ 1.2%) ($p = 0.0001$). There were no significant differences in the quantities of DDA and DEHYA extracted from all depths. Significantly larger quantities of unidentified polar degradates were formed in the top 10 cm (12%) compared with deeper soils ($\leq$ 2.6%) ($p = 0.001$). Fifty-seven percent of the applied radioactivity was unextractable (soil bound) from soil columns (sum of all depths). In the top 10 cm, 48% of the applied radioactivity was unextractable, and this quantity was significantly greater than in soils deeper than 10 cm ($\leq$ 4.8%) ($p = 0.0001$). The quantities of bound residues in the 10 to 20-cm depth were an order of magnitude below those formed in the top 10 cm (4.8%), and there were no significant differences in bound residue quantities among soils below 20-cm depth.

Mobility and Degradation of Metolachlor. Metolachlor (2-chlor-*N*-(2-ethyl-6-methylphenyl)-*N*-(methoxy-1-methylethyl)acetamide) is one of the most widely used herbicides in the Midwestern United States (12). This moderately soluble (530 mg/L at 20 °C) nonionizable

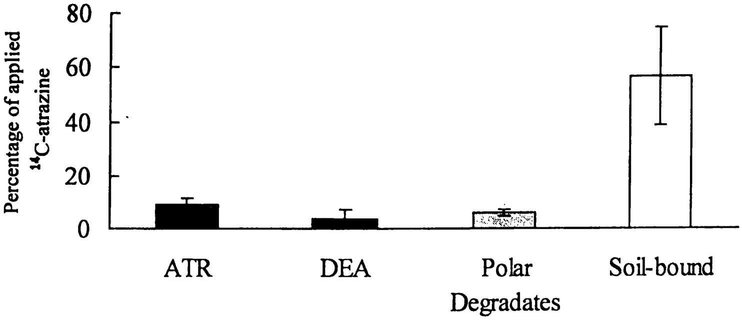

Figure 2. Percentages of applied ^{14}C as ATR, DEA, polar degradates, and soil-bound residues in the top 10 cm of intact soil columns treated with ^{14}C-ATR. Bars represent standard errors (n = 2).

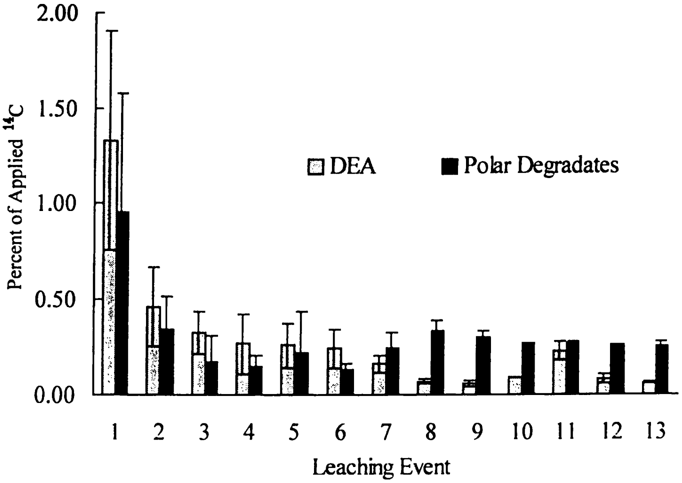

Figure 3. Percentages of applied ^{14}C-DEA recovered in leachate as DEA or polar degradates. Bars represent standard deviations of the mean (n = 2).

herbicide is primarily transported in the water phase and is more mobile and persistent than other chloroacetamide herbicides (13-16). Researchers have detected metolachlor in subsurface soils (2.28 m deep) (14,17), subsurface tile drain water, and groundwater (18-20). Based on the water solubility, sorption behavior, and moderate persistence of this herbicide, the United States Environmental Protection Agency (USEPA) has listed metolachlor as having a potential to leach through soil and contaminate groundwater (21). The following undisturbed soil column studies were conducted to evaluate the fate of radiolabeled metolachlor in the soil profile. The depth to which metolachlor leached in the soil and the quantity of metolachlor and metolachlor degradation products in the soil column and the leachate were determined.

Laboratory Preparation. Undisturbed soil columns were extracted from a pesticide-free field , prepared in the laboratory, and saturated with 0.005 M $CaSO_4$ as previously described (Figure 1A). The performance of each column and the reproducibility between the replicate soil columns were evaluated with a bromide ion tracer. A potassium bromide solution containing 17.5 mg of potassium bromide (9.903 kg/ha) was applied to the surface of each column. The soil columns were leached with 675 ml of ultrapure water to simulate 3.8 cm of rainfall. Leachates were collected in fractions, and the concentration of bromide ion in each fraction was measured using an ion-selective electrode.

Soil Treatment and Modification of the Soil Column for a Flow-through System. Technical grade metolachlor and [U- ring -^{14}C]metolachlor (100 μCi) were dissolved in water and uniformly applied to the surface of each soil column at the rate of 3.36 kg ai/ha. The treating solution was incorporated into the top 2 cm with a spatula, and glass wool was place over the top of each soil column to maintain the integrity of the surface. The top of the PVC pipe was sealed with a Plexiglas™ plate containing a polytetrafluoroethylene-covered neoprene stopper (#13) with three glass tube ports (Figure 1C). The center port was connected to a separatory funnel that allowed ultrapure water to be applied to the soil column weekly. The second port contained a charcoal trap that allowed air into the column and trapped organic volatiles from the headspace of the column. The final port led to a 0.1 N sodium hydroxide trap, followed by an Ultima Gold™ trap. A vacuum pump was used to create a suction that bubbled the contents of each column headspace through 0.1 N sodium hydroxide and Ultima Gold™ traps to absorb $^{14}CO_2$ and ^{14}C-organic volatiles, respectively. The radioactivity of the trapping solutions was measured with a liquid scintillation spectrometer. A vial containing a resazurin solution (several drops of a 4% resazurin solution in ethanol + water) was used to determine when the enclosed headspace of the soil column became anaerobic. When the column headspace became anaerobic, the headspace of the column was exchanged more frequently (22).

Leaching Study. Beginning 3 weeks after the treatment of the soil columns, each column was leached weekly for 12 weeks. The initial leaching of the columns was begun 3 weeks after the herbicide treatment to allow metolachlor to begin to degrade in order to observe the mobility of metolachlor and metolachlor degradation products through the soil profile. The leachates were collected, and the radioactivity in each leachate was determined by LSC.

Solid-phase Extraction (SPE) and Analyses of the Leachate. A portion of each leachate was vacuum filtered (glass fiber filter paper) and drawn through a solid phase extraction cartridge (Supelclean Envi-18™). The quantity of [^{14}C]metolachlor and [^{14}C]metolachlor degradation products in the methanol eluates were characterized by thin-layer chromatography (250-mm silica gel 60 F-254; hexane/methylene chloride/ethyl acetate (6:1:3, v/v/v) solvent system) (23) and autoradiography (X-Omat™ Kodak diagnostic film). The location of the non-radiolabeled standards were identified with an ultraviolet lamp (254 nm), and the percent of radioactivity characterized as metolachlor or metolachlor degradation products was measured by LSC.

Soil Extraction and Analysis. At the completion of the leaching study, soil columns were disassembled and divided into 10-cm sections. Three 50-g subsamples were taken from each 10-cm section and extracted three times with 150 ml of methanol/water (9:1 v/v). The quantity of metolachlor and metolachlor degradation products in the soil extracts were determined by thin-layer chromatography and autoradiography as described in the analysis of the leachates. Extracted soils were combusted with hydrolyzed starch in a Packard sample oxidizer (Packard Instrument Co., Downer's Grove, IL.) to determine the quantity of [^{14}C]soil bound residues. Radiolabeled CO_2 resulting from the combustion of the soil was trapped in Carbo-Sorb® E and Permafluor® V (Packard Instruments Co.) and the radioactivity in each sample was quantified using LSC. Percentages of [^{14}C]metolachlor mineralized to $^{14}CO_2$, leached through the soil column, and the amount remaining in the soil (bound and extractable) was calculated. Analysis of variance (ANOVA) was used to determine significant differences between metolachlor and metolachlor degradation products in the soil extracts and significant differences between soil-bound residues in the 10-cm sections of the extracted soil column.

Mobility and Degradation of Metolachlor. The initial metolachlor mobility studies were conducted with undisturbed soil columns similar to the deethylatrazine-treated columns (Figure 1B). At the completion of the analysis only 42% of the applied radioactivity had been recovered. Additional soil columns were treated with [^{14}C]metolachlor, and modifications were made to the soil columns to reduce chemical loss and improve the final mass balance. Despite the addition of the flow-through system (Figure 1C) and attempts to account for all radioactivity, the recovery of the applied ^{14}C in the modified soil columns was 44%. The results of this study are reported in percentage of recovered radioactivity.

Twenty-five percent of the recovered ^{14}C leached through the soil profile of the undisturbed soil columns. The quantity of radioactivity detected in the leachate gradually declined with the leaching events from 3.34% in the first leachate to 1.09% in the final leachate (Figure 5). Only trace amounts (<1%) of the recovered radioactivity were characterized as the parent compound, [^{14}C]metolachlor, in each of the leachates. At the completion of the leaching study, greater than 6,500 ml of leachate had been collected at the bottom of each column. The calculated concentration of metolachlor in the total leachate was 4.5 μg/L.

Metolachlor was degraded in the soil to a number of degradation products. Between six and eleven degradation products were detected in each leachate. Our findings are in agreement with those of (24) who detected metolachlor and six unidentified metolachlor metabolites in the leachate of greenhouse lysimeters. The presence of eight degradation products in the first leaching event indicates that some of the degradation products of metolachlor were as mobile or more mobile than the parent compound.

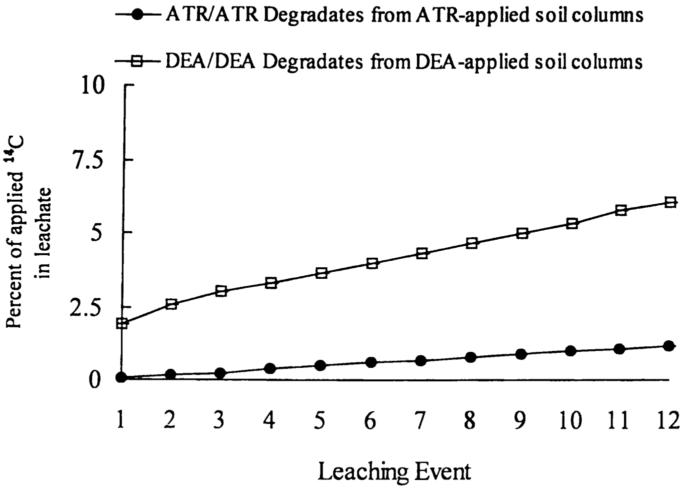

Figure 4. Radioactivity recovered in leachate from atrazine- or deethylatrazine-treated soil columns. Bars represent standard deviations of the mean (n = 2).

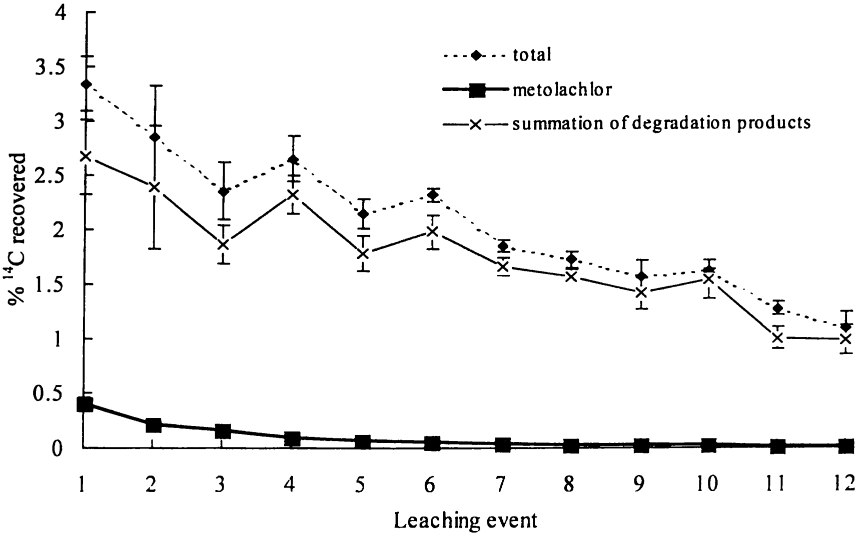

Figure 5. Metolachlor and metolachlor degradation products in the leachate of the undisturbed soil columns.

Distribution of Metolachlor and Metolachlor Degradation Products in the Soil Profile. Seventy-five percent of the recovered ^{14}C remained in the soil column. Surface soils (0-10 cm) contained more than five times the amount of radioactivity detected in any of the subsurface soils (10-60 cm) (Table I). The significantly greater ($p < 0.05$) percentage of radioactivity detected in the surface soils and the significant decline in the quantity of ^{14}C in the subsurface soils are similar to the findings of in the observations of (24,25) the fate of [^{14}C]metolachlor in greenhouse lysimeters and field lysimeters, respectively.

Soil-bound residues accounted for the largest percentage of radioactivity detected in the surface soils (Table I). Subsurface soils contained significantly less ($p < 0.05$) nonextractable residues than surface soils. The quantity of radioactivity bound to the surface soil was between eight and twenty-five times the amount found in the subsurface sections. The fate of agricultural chemicals in the soil and their potential to leach through the soil profile and contaminate groundwater is dependent on the persistence of the compounds and their sorption to the soil (26). Adsorption of metolachlor to soil is correlated with increasing organic carbon content ($r = 0.72$), percent clay ($r = 0.80$), and cation exchange capacity ($r = 0.94$) of the soil (9, 13, 27-29). Surface soils often contain greater quantities of organic matter than subsurface soils. Laboratory and greenhouse studies have reported metolachlor is weakly adsorbed and highly mobile in low-organic matter soils (<1% organic matter) (27). Examination of this Iowa soil reveals a 2.3% to 3.0% organic matter content in the soil from 0 to 45 cm. The presence of 48.7% of the recovered ^{14}C (31.9% nonextractable bound residues) in the top ten centimeters of our columns is believed to be the result, in part, of metolachlor and metolachlor degradation products adsorption to the humic fraction of this soil (30).

The greatest quantity ($p \leq 0.05$) of extractable [^{14}C]metolachlor and [^{14}C]metolachlor degradates were detected in the top 10 cm of the soil column (Table I). Less than 2% of the recovered ^{14}C was identified as [^{14}C]metolachlor in the soil extract of the surface soils, while 14% was identified as extractable metolachlor degradation products. Negligible quantities of metolachlor were measured in the soil extracts of the subsurface soils ($\leq 0.07\%$). Extractable metolachlor degradation products ranged from 0.88% in the 40-50 cm section to 3.49% in the 10-20 cm section.

Mineralization and Volatilization of Metolachlor. Ultima Gold™ traps and sodium hydroxide traps were used to collect organic volatiles and $^{14}CO_2$ produced from the mineralization of [^{14}C]metolachlor. Mineralization of [^{14}C]metolachlor to $^{14}CO_2$ was minimal. Less than one percent of the recovered ^{14}C was detected in the NaOH traps. Organic volatiles were not detected in the headspace of the columns.

Volatility and Mobility of Methyl Bromide. Undisturbed soil columns were used to study the volatility, mobility, and degradation of methyl bromide (MeBr) in soil (7,31). Two undisturbed soil columns (15-cm diameter x 38-cm length) were obtained from an agricultural field site (no previous pesticide history) near Ames, IA. Procedures for the collection, removal, and storage of the columns were previously described by (2) and in this chapter. Additional soil samples were collected at the same depths as the column to determine the soil physicochemical properties. A composite of these soil samples consisted of sandy clay loam soil with a pH of 5.4 and 54% sand, 25% silt, 21% clay, and 2.5% organic matter.

Table I. Distribution of [^{14}C]metolachlor and [^{14}C]metolachlor degradation products in undisturbed soil columns

	Percent of recovered ^{14}C (± SE)[a]					
Soil depth:	0-10 cm	10-20 cm	20-30 cm	30-40 cm	40-50 cm	50-60cm
Extractable residues						
Metolachlor	1.30 A (0.102)	0.02 B(0.007)	0.06 B (0.003)	0.06B (0.009)	0.07 B(0.016)	0.05 B(0.011)
Degradation products	14.0 A (0.76)	3.49 B(0.19)	2.38 C (0.078)	1.55D (0.055)	0.88 D(0.098)	0.96 D(0.086)
Soil-bound residues	31.9 A (2.1)	3.71 B(0.12)	2.86 B (0.16)	1.84B (0.088)	1.32 B(0.044)	1.25 B(0.039)
Total[b]	48.7 A (2.07)	8.35 B(0.73)	6.09 B,D(0.25)	5.22C,D(0.43)	3.62 C,D(0.69)	3.07 C(0.51)

[a] Means in each row followed by the same letter are not statistically different ($p=0.05$).

[b] Summation of metolachlor, metolachlor degradation products, and soil-bound residues.

Undisturbed soil columns were prepared for laboratory studies as described by (3,6) and in this chapter (Fig. 1A-1B). Modifications were made to collect the MeBr that volatilized from the soil (Fig. 1D) (7). The PVC pipe on the exterior of the column was longer than the soil column to ensure sufficient headspace for the addition of an activated carbon trap. A Plexiglas™ plate with three openings was mounted to the top of each PVC pipe and sealed with silicon rubber adhesive sealant. These openings were sealed with polytetrafluoroethylene-covered neoprene stoppers containing either a granular-activated carbon trap, resazurin trap, or glass tube sealed with a septum (for addition of water). Granular-activated carbon traps were suspended in the headspace of each column to adsorb MeBr that volatilized from the soil. Each trap consisted of 8 g activated charcoal wrapped in 5 x 5-cm, 100% cotton net (1-mm mesh). Resazurin traps (0.5 ml 4% resazurin in ethanol, with 4.95 ml deionized water) were used to indicate if the column headspace was becoming anaerobic. Soil columns were initially saturated with 0.005 M $CaSO_4$ then drained to field capacity as previously described in this chapter. Four 500-mL increments of deionized water were leached through the columns to determine the naturally occurring bromide ion (Br^-) background concentration.

Soil Treatment and Leaching. Liquid MeBr (at 0.57 kg/m3, or 1 lb/yd^3) was applied to the soil surface, and the columns were immediately sealed. Soil columns were incubated at 24 ± 1 °C for 48 h to allow this fumigant to penetrate the soil and reach an equilibrium between the air/soil/water. After the 48-h equilibration period, MeBr-fumigated columns were place in column stands, maintained at 24 ±1 °C, and leached weekly (for 23 weeks) with 500 mL deionized water to represent 2.5 cm of rainfall (7). Leachates were collected at the bottom of the columns and analyzed for MeBr and its degradation product, Br^-.

Collection and Analysis of Volatilized Methyl Bromide. Forty-eight hours after the application of MeBr, activated carbon and resazurin traps were suspended in the headspace of each soil column. Carbon traps were replaced periodically and used to determine the amount of MeBr in the headspace of the column. Upon removal, these traps were placed in 45-mL glass bottles equipped with screw caps and polytetrafluoroethylene-lined septa and stored at -60 °C until analysis. The headspace of these bottles was analyzed prior to the desorption of MeBr from the carbon. Procedures used to desorb MeBr from the carbon traps were modified from (32). Two gram-carbon subsamples from each trap were placed in 7-mL glass vials and sealed with a polytetrafluoroethylene-lined septa. Three mL of air was evacuated from the vials with a gas-tight syringe and replaced with 3 mL benzyl alcohol (Fisher Scientific, Pittsburgh, PA). Samples were warmed to 110 °C for 15 minutes and the headspace was analyzed by gas chromatography (GC). The quantities of MeBr detected in the headspace of the bottles and desorbed off the carbon were considered in the final calculation of MeBr that volatilized from the soil.

Procedures for the analytical standards and analysis of sample and standard headspace were modified from (32). Methyl bromide standards were made in benzyl alcohol, stored at -60 °C, and replaced every 2 weeks. Samples were analyzed on a Varian 3740 gas chromatograph equipped with a ^{63}Ni electron-capture detector. The glass column (0.912 m x 2.0 mm i.d.) was packed with 100/120 mesh Porapak Q (Supelco Inc., Bellefonte, PA) on Carbopack with a carrier gas consisting of ultrapure nitrogen (26 mL/min). Injector, column, and detector temperatures were 170 °C, 140 °C, and 350 °C, respectively. Peak heights were used to construct a calibration curve and quantitate the samples.

Analysis of Leachate. Soil column leachates were analyzed for MeBr and Br^- by using GC headspace analysis as described above and a bromide-specific electrode attached to pH meter (Fisher Scientific, Pittsburgh, PA). Br^- standards were prepared with NaBr, deionized water, and 5 M $NaNO_3$ (ionic strength buffer). Calibration curves were constructed from the standards and used to determine the sample concentrations.

Soil Extractions and Analysis. At the completion of the study, undisturbed soil columns were cut into 5-cm increments and analyzed for MeBr and Br^- residues. Three 10-g subsamples from each soil profile were placed in 45-mL glass vials, and the headspace was analyzed on a GC as described above. These soil samples were then extracted with 20 mL deionized water by mechanical agitation and centrifugation. The supernatant was removed and analyzed for Br^- using a bromide-specific electrode.

Volatility, Mobility, and Degradation of Methyl Bromide. MeBr volatilized rapidly from the soil. The flux of MeBr from the undisturbed soil columns is shown in Figure 6. Greater than 75% of the MeBr flux occurred within 48 h after the fumigation period. After 7 days, MeBr was not detected in the soil column headspace. The volatilization of MeBr from our undisturbed soil column study was comparable to the MeBr field study results reported by (31,33-34). Anderson et al., (31), also observed greater than 75% of the MeBr flux occurred within 4 days after MeBr application. Negligible quantities of soil gas MeBr were detected after 7 d (31,33).

Soil column leachates from each rain event were analyzed for Br^- and MeBr. Within the first rain event following the MeBr fumigation, Br^- increased from a background level of 0.01 µg/g to 0.4 µg/g (Figure 7) The concentration of Br^- in the leachate continued to increase, peaked at 3 weeks (4.3 µg/g), and gradually decreased with subsequent rain events. A total of 28.8 µg/g Br^- leached through the soil column, which represents > 5% of the MeBr initially applied. MeBr was not detected in any of the soil column leachates throughout the 23-week study. Wegman et al. (35) detected MeBr and Br^- in drainage water from fumigated glasshouse soils. They observed a sharp increase in the concentration of Br^- during the initial irrigation of greenhouse soils, followed by a steady decrease. The increase of Br^- and the absence of MeBr in the soil column leachates indicate MeBr will degrade in the soil and will not leach through this soil profile.

After the final rain event, soil columns were divided into 5-cm fractions and analyzed for MeBr and Br^-. Residuals of this fumigant and the metabolite were not detected in the soil profile. Levels of Br^- were similar to control (untreated) soil samples. Persistence of MeBr in soil appears to be low, primarily due to its rapid volatilization, as well as biological and chemical degradation. Based on these results MeBr would not be expected to contaminate groundwater unless preferential flow was involved.

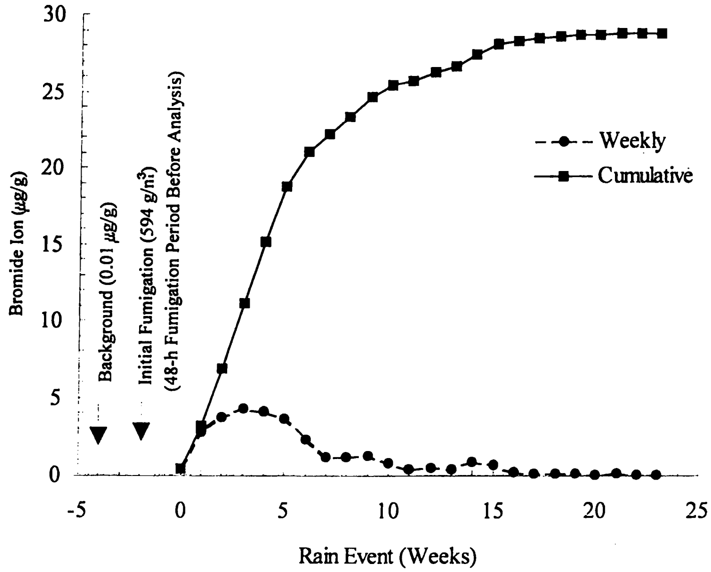

Figure 6. Volatility of methyl bromide in undisturbed soil columns following a 48-h fumigation period. Data points are the mean ± one standard deviation.

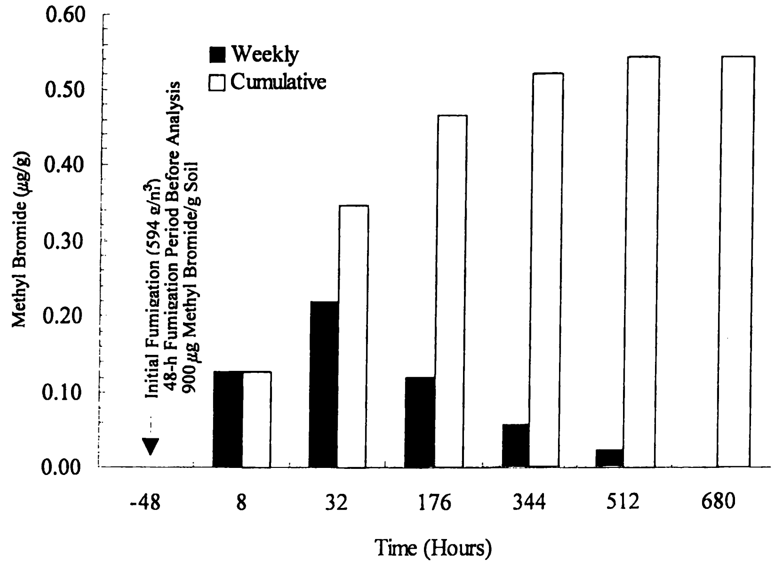

Figure 7. Bromide ion breakthrough from an undisturbed soil column treated with methyl bromide. Soil columns were leached weekly after the 48-h fumigation period.

Pesticide Adjuvants.

Pesticide applications invariably include the use of various adjuvants in the commercial formulations. This broad category can include solvents, emulsifiers, sticking agents (adhesives), UV-light protectants and dyes, among others. They are mostly considered to be inert ingredients, but their environmental fate should also be addressed. Most of them have other industrial uses and, hence, other environmental inputs.

Ethylene glycol and propylene glycol have been used as solvents in pesticide formulations as well as antifreeze in vehicles and deicing agents for airplanes and runways. Their environmental impact is often expressed as an excess nutrient input into bodies of water, leading to a eutrophic anoxic system in which fish and other species with high oxygen requirements die. Their degradation and mobility have not been previously investigated in a soil column experiment.

Effects of Plants on the Degradation of Pesticide Adjuvants in the Intact Soil Column. Rhizosphere is the region of soil directly influenced by the roots. Plant roots secrete energy-rich exudates (sugars, amino acids, vitamins, and keto acids) and mucilages (polysaccharides) that support large and diverse populations of microorganisms. Root-influenced soils have a greater microbial biomass (10 to 100 times) and activity than bulk soils; therefore, enhanced degradation of organic compounds may occur in the rhizosphere (36-39). In addition, the interaction between plants and their associated microbial communities is mutually beneficial for both types of organisms. Soil microorganisms have a positive influence on plants by 1) solubilizing inorganic nutrients and secreting organic compounds (gibberellins, auxins, amino acids, and vitamins) that stimulate plant growth and 2) potentially deterring plant pathogens through competition and production of antibiotics (36, 38, 40).

Vegetation can enhance the removal of human-made organic compounds and pollutants in soil environments by microbial degradation in the rhizosphere and plant uptake (41,42). Previous research has shown enhanced degradation of industrial chemicals such as trichloroethylene (43) polycyclic aromatic hydrocarbons (44), and petroleum (45) in the rhizosphere soil as compared to root-free soil. Increased mineralization of the pesticides parathion (46) and carbofuran (47) has been reported in the rhizosphere of rice plants. Hsu and Bartha (48) noted similar results for parathion in the bean rhizosphere. Accelerated mineralization of pesticides has also been found in the rhizosphere of plants from pesticide-contaminated sites. Anderson et al. (49) observed greater microbial biomass and enhanced degradation of atrazine, trifluralin, and metolachlor (after 14 d) in the rhizosphere soil of herbicide-resistant *Kochia sp.* in comparison to nonrhizosphere and sterile soils, respectively. In addition to enhanced degradation in the rhizosphere, plants may take up contaminants as part of their transpiration stream (41). Lee and Kyung (47) monitored the uptake of fresh and aged carbofuran residues by rice plants. Approximately 60 to 70 % of the ^{14}C detected in the shoots was the intact parent compound in both the freshly applied and aged soils. Anderson and Walton (50) studied the fate of [^{14}C]TCE in soil-plant systems collected from a contaminated site. They reported that 1 to 21% of the recovered radiocarbon (depending on the plant species) was detected in the plant tissues, particularly in the roots. Vegetation may play a vital role in reclaiming polluted ecosystems and preventing further contamination by enhancing degradation and uptake into tissues, thereby reducing migration to surface waters and groundwater aquifers.

Effect of Vegetation on Mobility of Pesticide Adjuvants. Vegetated undisturbed soil columns were used to study the influence of plants on the mobility of propylene glycol (PG) and ethylene glycol (EG) through the soil profile. High concentrations were applied to nonvegetated and vegetated undisturbed soil columns to simulate spills of these solvents used as antifreezes, airplane deicing agents, and pesticide adjuvants.

Undisturbed soil columns (15-cm x 38-cm length) were collected from an agricultural field site and prepared for laboratory studies as previously described in this chapter (Figure 1A) and by (2,3).

Eight soil columns (4 each) were planted with alfalfa (*Medicago sativa*) or rye grass (*Lolium perenne L.*) (Figure 1E). Nonvegetated and vegetated columns were maintained in a greenhouse (25 °C, 16:8 light:dark) for 4 months to allow sufficient growth of the plants. Water was added to the columns as needed. Roots of *M. sativa* and *L. perenne* were observed through the clear perforated Plexiglas™ bottom of the columns. This indicated that *M. sativa* and *L. perenne* roots were established through the length of the columns. Following the four-month growth period, soil columns were saturated with 0.005 M $CaSO_2$ (2), then drained to field capacity.

Soil columns were moved to an incubator set at 25 °C, and the temperature was slowly decreased (approximately 3 °C/24h) to 10 °C to represent spring conditions. Soil columns were maintained at 10 °C with a 16:8 light:dark cycle for 96 h prior to the treatment to acclimate plants to this temperature. During this 96-h time period, soil columns were leached with 400 ml deionized water. These leachates were analyzed on a gas chromatograph equipped with a flame ionization detector (GC-FID) and with a bromide-specific electrode attached to a pH meter (Fisher Scientific, Pittsburgh, PA) to determine background levels of propylene glycol and Br^-, respectively. A KBr tracer was applied to the soil surface and leached through the soil columns with deionized water. Breakthrough curves were determined for each column by analyzing the quantity of Br^- in the leachate. Br^- standards were prepared with NaBr, deionized water, and 5M $NaNO_3$ (ionic strength buffer). Calibration curves were constructed from the standards and used to determine the sample concentrations (8).

Soil Treatment and Leaching. Propylene glycol (Fisher Scientific, Fair Lawn, NJ) solution (1.76 ml PG/ 364 ml water) was applied to the soil surface. Twenty-four hours after the treatment, soil columns were leached with 400 ml deionized water daily. Water was applied to the columns in four 100-ml increments. This application caused a temporary pooling of water each time. Soil columns were leached repeatedly throughout the studies (see Figures 8 & 9). Leachates were collected at the bottom of each column and analyzed on a gas chromatograph (GC) to determine the quantity of PG and EG that moved through the soil profile. Samples were stored in a freezer until the analysis.

Analysis of Leachates. Undisturbed soil column leachates were analyzed following procedures modified from (51). Propylene glycol and ethylene glycol standards were made every two weeks in deionized water and stored in a freezer. Leachate samples were analyzed on a Varian model 3740 GC (Varian Associates, Sunnyvale, CA, USA), equipped with a flame ionization detector (FID) and 2.7 m x 2 mm (i.d.) glass column containing 5% Carbowax 20M on 100/120 mesh Supelcoport^R (Supelco Inc., Bellefonte, PA). Ultrapure nitrogen (99.9%) was used as the carrier gas at a flow rate of 20 ml/min. The injector and oven

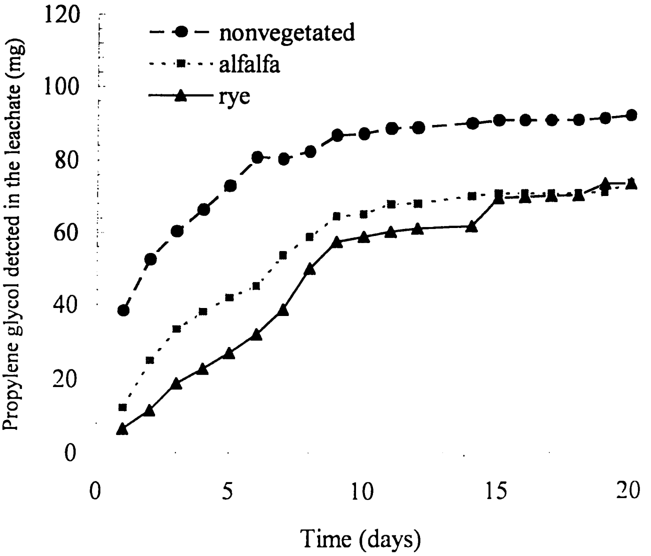

Figure 8. Concentration of propylene glycol detected in the leachate of vegetated and nonvegetated soil columns.

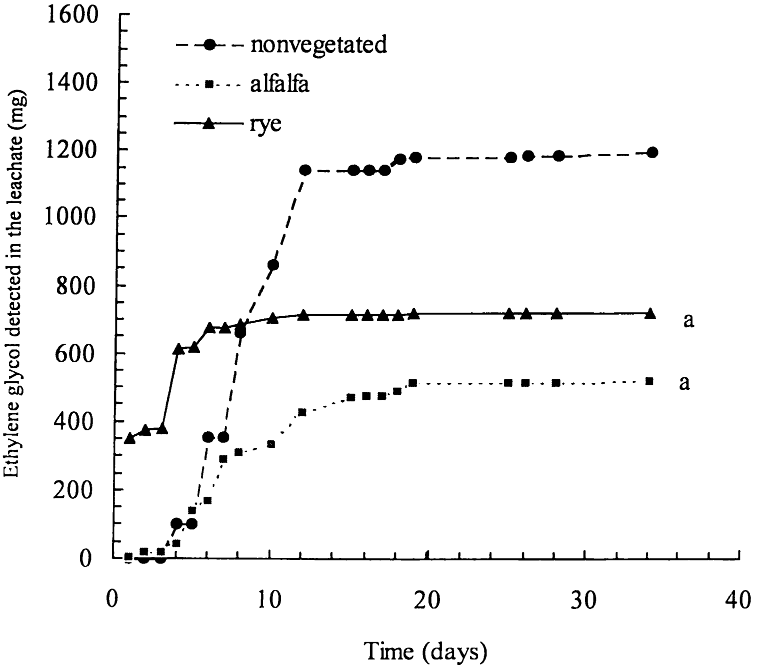

Figure 9. Cumulative concentration of propylene glycol detected in the leachate of vegetated and nonvegetated soil columns.

temperatures were 250 °C and 160 or 200 °C. Propylene glycol samples were also analyzed on a Shimadzu GC-9A GC-FID (Shimadzu Corp., Kyoto, Japan) equipped with a 5% Carbowax 20M packed column (1.2 m x 3 mm i.d.). The carrier gas was helium, and the injector and oven temperatures were 300 °C and 160 °C, respectively. Peak heights were used to construct each calibration curve and to quantitate the glycol in the samples. All the standard curves had correlation coefficients exceeding 0.990. One-way analysis of variance (ANOVA) and the least squared means were used to test for significant differences among the treatments (52).

Influence of Vegetation on the Mobility of Glycols in Soil Columns. Propylene glycol and ethylene glycol were detected in the leachates of all the soil columns studied (Figure 8 and 9). The greatest PG concentrations occurred within the first four leaching events and continued to decrease with time. Approximately 53 to 86% of the recovered PG was detected in the leachates within 7 d.

Greater than 500, 300, and 200 μg/ml EG was noted in leachates of the nonvegetated, *M. sativa* and *L. perenne* soil columns. After 10 days, 64 to 92% of the recovered EG had leached through the soil columns. Movement of PG and EG through the soil profile depends on its properties and adsorptive characteristics, soil characteristics, soil temperature, and the quantity and frequency of runoff or precipitation (53).

Previous research has shown EG does not adsorb to soil (51). Lokke (51) reported little or no adsorption of EG to sandy till, muddy till, or clayey soils. Propylene glycol and ethylene glycol are water soluble and appear to be mobile within the 38-cm soil profile.

Results from this study indicate vegetation reduced the quantity of PG and EG that moved through the soil profile. Leachates from the vegetated soil columns contained significantly ($p = 0.05$) less PG than leachates from the nonvegetated columns (Figure 8). Measured quantities of 91.5, 73.0, and 73.0 mg of PG were detected in leachates of nonvegetated, *M. sativa*, and *L. perenne* soil columns, respectively. Similar results were noted with the EG-treated soil columns (Fig. 9). The total quantity of EG that infiltrated through nonvegetated, *M. sativa,* and *L. perenne*, and soil columns was 1195, 519, and 722 mg, respectively. The results of the nonvegetated column shown in Figure 9 contain only one replication due to the loss of the second nonvegetated soil column. Less EG was detected in the leachate from *M. sativa* soil columns than *L. perenne*, but they were not significantly ($p = 0.05$) different. Plants can decrease the concentration of PG and EG in soil and reduce their movement through the soil profile to groundwater by plant uptake, enhanced degradation in root-associated soils, and reduction of the soil water status (41). Results from previous research show enhanced degradation of EG and PG in the *M. sativa* and *L. perenne* rhizosphere soils compared to nonvegetated soil (54). In the current study, we observed a 9 to 12% decrease in the quantity of water that leached through vegetated soil columns relative to the nonvegetated soil columns, together with even greater reductions in the percentages of PG and EG that leached in the nonvegetated columns. Overall, vegetation can clearly reduce the leaching of PG and EG through the soil profile.

Comparisons With Other Methods

Incubation Studies. While soil column studies provide important information on the mobility of parent compounds and degradation products, comparisons of data from pesticide-applied columns to that of controlled soil metabolism studies gives a better understanding of the fate of the compounds. In studies conducted using intact soil columns, such as described in this chapter, the presence of degradation products at various depths may be due either to movement of degradation products formed in upper layers or to the degradation of the parent compound once it has reached a particular depth. This is not the case in controlled soil metabolism studies using contained soils from various depths, where the presence of degradation products cannot be due to movement from another depth. Soil metabolism studies with a time series of analyses can also give information on half-lives for applied pesticides.

From the ATR-applied soil column study (3), it was noted that DEA was present in subsurface soils which could be due not only to degradation of ATR in all depths, but also to movement after formation in upper layers. DEA was more mobile than ATR in the soil column studies (3, 6). The comparative fate of ATR and DEA in surface (0 to 30 cm) and subsurface (65 to 90 cm) soils was studied in the laboratory (55). The concentration of DEA arising from ATR degradation in subsurface soil increased 3-fold from a 60- to 120-d incubation period. The half lives of DEA and ATR were significantly greater in subsurface soils than in the surface soils. However, in soil from the 90- to 120-cm depth (held at -33 kPa soil moisture tension), the half-lives for DEA and ATR were 178 and 161 d, respectively (55, 56).

Soil Thin-layer Chromatography. Studies on the mobility of pesticides have been carried out by using a method of thin-layer chromatography (TLC) that incorporates a thin film of soil onto a glass plate. Soil TLC (STLC) plates applied with radiolabeled pesticides are then submitted to ascending chromatography by placing the plates in developing chambers containing water as a mobile phase. The differential affinity of a pesticide for soils of various characteristics and water can easily and economically be determined. While the assessment of pesticide mobility in large, intact soil columns is more true to field conditions, space requirements, time, and cost are considerations for running multiple columns of various soil characteristics. Concerns, however, with using STLC are that no indication of preferential flow can be obtained, and in the process of making STLC plates, pulverization of soil can alter soil characteristics such that care must be taken with inferences to the real world.

In comparing the ATR- and DEA-applied soil column studies with an STLC study, all conducted in this laboratory, it was noted that relative mobilities of ATR and DEA were consistent. The relative mobilities of ATR, DEA, other pesticides, and degradates were determined in an STLC experiment that used soils from the surface (0 to 30 cm) and subsurface (65 to 90 cm) from ten soil types (2 depths, 5 locations) of Iowa (57). In this study, DEA was the most mobile compound in 8 of the 10 soils. These results agree with the soil column studies in which DEA was recovered in greater quantities in leachate than was ATR (Figure 4).

Field Box Lysimeters. With the use of field box lysimeters, it is possible to study the fate of pesticides under field conditions, while maintaining a somewhat contained system. Box-type lysimeters (Figure 10) had been constructed using polyethylene sheets for sides and bottom that were assembled by using stainless-steel bolts to secure aluminum angle-iron corners onto

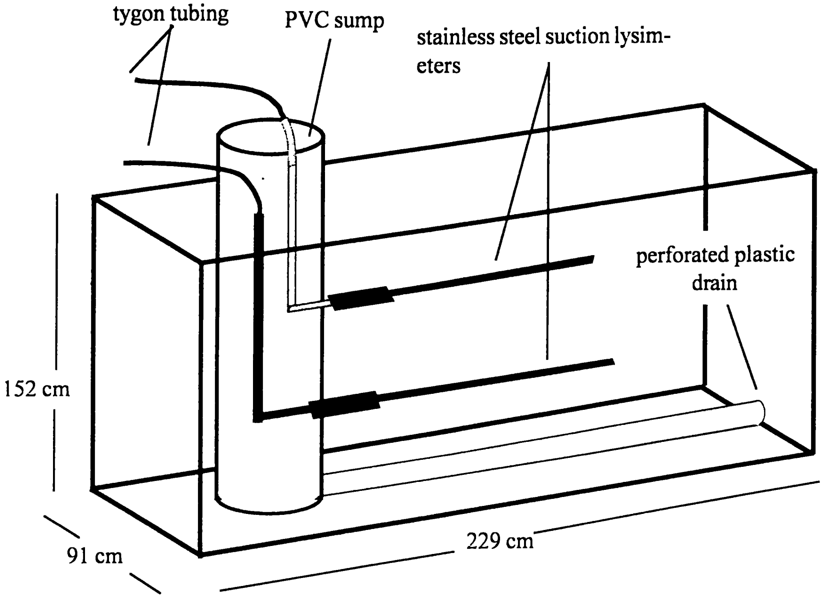
tygon tubing
PVC sump
stainless steel suction lysimeters
perforated plastic drain
152 cm
91 cm
229 cm

Figure 10. Field box lysimeter used to study pesticide concentrations in leachate and in soil water.

the sheets (58). The corner seams were treated with silicone sealant to make them waterproof, and styrofoam sheets (2.5-cm thick) were placed against each side. Heavy-duty duct tape was used to join each foam sheet, and a 0.5 mm-thick box-shaped, impermeable plastic liner, with the same shape and dimensions as the lysimeter box, was placed inside each lysimeter, pulled tightly over the styrofoam sheets, and attached to the outside of the lysimeter with duct tape. The sides of the lysimeter extended above the soil surface. Through the use of a grave-digging machine, the soil profile was excavated to make a hole that measured 234 cm by 92 cm by 137 cm. For the top 60 cm, soils were separated into 15-cm layers, and for soils between 60 and 150-cm depth, soils were separated into 30-cm layers. A bentonite layer (5-cm thick) was placed at the bottom of each excavated area. The lysimeter box was lowered into the hole, and the gaps between the lysimeter and the soil were fill with bentonite. A drainage-tile sump apparatus was installed, and the soil was replaced in the lysimeter layer by layer, according to the original vertical soil profile. Two stainless steel suction lysimeter tubes were installed, one on each side of the sump. One suction tube was installed at a depth of 60 cm and the other at 90 cm A two-year study of atrazine mobility and degradation in box lysimeters showed that rate of application had an influence on the detection of residues in water collected in the soil profile (59, 60).

This approach to studying the mobility of pesticides is advantageous in that one can conduct rain simulations over the lysimeters, use various cropping systems, monitor pesticide movement to tile drains, and determine concentrations in soil water by using the suction lysimeters. With the excavation of the soil profile, however, it takes some time to reestablish soil structure, and the box lysimeters are too large to remove to analyze.

Conclusion

It is clear that several of the advantages of the lysimeter as an experimental unit are also expressed in the intact soil column. The focus on intact soil columns in this chapter provides some degree of comparison in the techniques. Both maintain the crucial capacity to *integrate the fate of the pesticide*, measuring both degradation and mobility of the parent compound and transformation products. As analytical methods become more sophisticated, as public concern over pesticides grows, and as requirements for pesticide registration data expand, it is important that our understanding of pesticide degradation and movement in the environment continues to advance. The advancement of our knowledge is, to a large degree, limited by the tools we possess to make the assessments of the behavior of agrochemicals in our environment. It is therefore imperative that we constantly strive to develop and improve our methodology, such as the lysimeter approach, to aid in the production and protection of a safe and bountiful food supply, while affording protection of the environment.

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Chapter 8

Use of Field Lysimeters To Determine ^{14}C-Dicamba Persistence and Movement in Soil

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Persistence and movement of ^{14}C-dicamba was determined in the top 90 cm of a clay loam soil in 30 x 100 cm intact soil lysimeters in the field during a 16-mo period. All of the applied ^{14}C was still in the profile 1 month after application (MAA). Although 97% was still in the top 20 cm depth, small amounts of ^{14}C (<0.1% of applied) were found at the 80-90 cm depth. This was the only time during the study that ^{14}C was found this deep. Of the 89% of the applied ^{14}C remaining at 1 MAA in the top 10 cm of soil, 6% was dicamba and 27% was 3,6-dichloro-2-hydroxybenzoic acid. At 6 MAA, 50% of applied ^{14}C was still present in the soil profile, 99% of which was in the top 20 cm of soil. Of the 54 % of the applied ^{14}C remaining in the top 10 cm of soil, 11% was 3,6-dichloro-2-hydroxybenzoic acid, and we could not confirm any dicamba.

In order to assess the potential impact of pesticide use on environmental quality, it is important to understand the simultaneous transport and transformation of the pesticide in the field. However, in most traditional field studies, only the parent molecule and at times selected metabolites are monitored. Metabolites monitored are often dependent on the ease of analysis

Because of dicamba's (3,6-dichloro-2-methoxybenzoic acid) low sorption in soils at normal pH levels (*1-3*), it is a potentially highly mobile herbicide (*4-6*). However, mitigating the sorption effects on mobility is the fact that dicamba can be rapidly degraded (*7-9*). Degradation products include 3,6-dichloro-2-hydroxybenzoic acid (3,6-DCSA), 3,6-dichloro-5-hydroxy-2-methoxybenzoic acid (5-HO-dicamba), 3,6-dichloro2,5-dihydroxybenzoic acid (2,5-diOH), and CO_2 (*10*). While there is research on environmental fate and behavior of dicamba in soil, there is little information on formation and movement of its metabolites in the field.

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The use of ^{14}C-labeled chemical in the field would facilitate determination of a mass balance of the chemical with respect to the simultaneous leaching and degradation. In order to use a ^{14}C-labeled pesticide in the field, the ^{14}C usually must be contained in a confined area. Very few laboratories have the resources to construct a model system of lysimeters similar to that developed by Dr. Fritz Führ at the Institute of Radioagronomie of the Nuclear Research Centre, Jülich, Germany, which has received international recognition as the state-of-the-art methodology to investigate the fate of pesticides in the environment. Research on a variety of pesticides has been conducted at this facility.

Previously, we have also successfully used large field lysimeters (0.3 m diam by 0.9 to 1.0 m deep) to determine the degradation and movement of ^{14}C-atrazine and its major metabolites in three soils in Minnesota (*11-13*). These lysimeters were inserted into the soil, ^{14}C-herbicide applied to the soil, and corn plants grown in and around the lysimeters. Thus, throughout the experimental period, the soil and applied chemical were subjected to natural temperatures and rainfall under normal corn production practices. We now report the use of similar field lysimeters to determine the fate and behavior of ^{14}C-dicamba in soil.

Materials and Methods.

Chemicals and solvents. Dicamba (99 % purity) and 5-HO-dicamba (99% purity) were obtained from ChemService (West Chester, PA) and 3,6-DCSA (99% purity) from Sandoz Crop Protection Corporation (Des Plaines, IL) [Note: Mention of a vendor or proprietary product does not constitute a guarantee or warranty on the part of USDA or the University of Minnesota and does not imply its approval to the exclusion of other products or vendors that may also be suitable]. ^{14}C-uniformly ring-labeled dicamba (106 Mbq mmol^{-1}) (radiochemical purity, > 98.5%) was purchased from Pathfinder Laboratories (St. Louis, MO 63178). Technical grade methanol and dichloromethane, HPLC grade acetonitrile, glacial acetic acid, $CaCl_2$, HCl, and microcrystalline cellulose were used as received.

Field procedures. The experiment was conducted at University of Minnesota Southern Experiment Station, Waseca, MN on Webster clay loam soil (Table I). Southern Minnesota has a mean annual temperature of 6 °C, and soils are frozen for 4 months. Annual precipitation is 640 mm, and pan evaporation is 1000 mm (*14*). Sections of 0.3-m diam polyvinyl chloride (PVC) pipe (wall thickness 1.2 cm), 0.9 m long, with one end sharpened, were coated with vegetable oil and inserted into the soil using a front end loader tractor 8 mo prior to start of the experiment. Compression of the soil inside the columns was less than 5 cm. Additional columns 0.7 m deep were inserted into the soil and then equipped with a water collection device to monitor ^{14}C movement out of the bottom of the column, details of which have been previously reported (*11*). In brief, the collection device was a hollow glass block with holes drilled in the surface. After excavating one side of the lysimeter and underneath the column, the glass block was secured against the bottom of the column with glass wool between the soil and glass block. A water collection tube, one end of which was inserted into the block, was brought to

Table I. Selected physicochemical properties of Webster clay loam soil.

Soil depth	pH	Organic carbon	Clay (<2 μm)	Silt (2-50 μm)
cm		%		
0 - 10	6.2	4.3	33	38
10 - 20	6.1	3.8	33	37
20 - 30	6.4	3.5	34	37
30 - 60	6.8	1.0	39	40
60 - 90	7.4	0.3	27	31

the soil surface outside the column. The soil was then replaced. Water was removed from the glass block by applying a vacuum to the sampling tube. Sampling was conducted following each rainfall or irrigation event and prior to column removal.

After insertion of the lysimeter, an additional 9-cm section of pipe was attached to each column to prevent runoff from the treated soil. Access to the plots was restricted by a fence. ^{14}C-dicamba in 5 mL methanol was applied to the center 10-cm-diam area of the column, 2.5 cm below the soil surface. Following ^{14}C application, three corn seeds (*Zea mays* L.) were planted in the center of each column. Corn was planted in the rest of the plot area at 60,000 seed ha^{-1}, and dicamba was applied to the entire plot area at 0.7 kg ha^{-1}. After emergence, corn was thinned to one plant per column. Irrigation was applied to the columns in 2.5-cm increments as needed.

Three soil columns were removed at each sampling time: immediately following, and 1, 2, and 6 mo after ^{14}C-dicamba application (MAA). Soil columns were sectioned into 15-cm depth increments and the soil and corn plants were stored at -15 °C until analyzed. During the second year, three columns were removed at both 12 and 16 MAA. Following the 12 MAA sampling, three corn seeds were planted into each of the remaining columns. After emergence, corn was thinned to one plant per column. Corn was planted in the rest of the plot area at 60,000 seed ha^{-1} and dicamba was applied to the entire plot area at 0.7 kg ha^{-1}. After emergence, corn was thinned to one plant per column. Irrigation was applied to the columns in 2.5-cm increments as needed. At 16 MAA the columns were removed and processed as previously described.

Laboratory procedures. Soil was extracted sequentially with 0.01 M $CaCl_2$, acetonitrile:H_2O:glacial acetic acid (70:27:3 v:v:v), and 1 N HCl. Acetonitrile was evaporated and the three aqueous extracts were extracted with dichloromethane (DCM). DCM was evaporated and residues redissolved in methanol. ^{14}C-residues were separated by HPLC, and fractions corresponding to dicamba, 5-HO-dicamba, and 3,6-DCSA, were collected and radioactivity analyzed by liquid scintillation counting (LSC) using a Packard Tri-Carb scintillation analyzer (Packard Instruments, Downers Grove, IL). ^{14}C eluting before and after the above chemicals are termed nonpolar and polar metabolites, respectively. After extraction, soil was combusted, as described later, to determine unextractable ^{14}C.

For total ^{14}C in soil, 3 subsamples were combusted from each depth and replicate using a Packard 306 Sample Oxidizer (Packard Instruments, Downers Grove, IL). Soil (0.4 g) was mixed with 0.1 g microcrystalline cellulose and placed in a paper cone and combusted for 2 min. CO_2 was trapped in CARBOSORB and then mixed with PERMAFLUOR E+ (Packard Instruments, Downers Grove, IL). Radioactivity was determined by LSC. The efficiency of oxidation was determined to be 95 ± 3 %.

HPLC analyses were performed on a HP1090 HPLC (Hewlett Packard, Avondale, PA) with a Supelcosil ABZ+ column (4.6 mm x 25 cm, 5 μm) (Supelco, Bellefonte, PA) equilibrated at 50 °C. The mobile phase was a gradient elution starting at 50:50 0.025 M KH_2PO_4 (pH = 2.35):acetonitrile to 20:80 0.025 M KH_2PO_4 (pH = 2.35):acetonitrile over 20 min at a flow rate of 1.75 mL min^{-1}. Detection of dicamba, 3,6-DCSA, and 5-HO-dicamba was determined at 205 nm, and retention times were determined using high purity standards. Samples were then collected as fractions in separate vials dictated by retention times of dicamba, 3,6-DCSA, and 5-HO-dicamba standards, and ^{14}C was determined by LSC.

Results and Discussion.

Total ^{14}C Dissipation. Recovery of total ^{14}C remaining 1 mo after application (MAA) was 100% of that applied (Table II). Total ^{14}C at 2 MAA was 62 % of applied at 2 MAA and decreased to 56 - 49% at 12 - 16 MAA. A small amount (< 3%) of ^{14}C was lost due to plant uptake. Although dicamba is nonvolatile, potential losses were kept to a minimum by applying the ^{14}C-dicamba below the soil surface. The rest of the ^{14}C was assumed to be lost by mineralization to $^{14}CO_2$ rather than by leaching out of the lysimeter, which is discussed below.

Table II. Distribution of ^{14}C in soil profile as a function of time.

	Months after application					
Depth	0	1	2	6	12	16
cm	% of applied ^{14}C					
0-10	99.9 ± 9.2[a]	88.8 ± 4.0	56.5 ± 1.6	53.9 ± 8.3	47.3 ± 9.7	43.2 ± 14.8
10-20	0	8.4 ± 4.8	3.3 ± 1.1	5.4 ± 1.8	5.8 ± 3.8	5.2 ± 0.8
20-30	0	1.7 ± 0.9	1.9 ± 1.6	0.9 ± 0.5	2.0 ± 0.5	0.9 ± 0.6
30-40	0	1.8 ± 1.7	0.5 ± 0.2	< 0.1	0.5 ± 0.2	0.1 ± 0.1
40-50	0	0.5 ± 0.1	< 0.1	0	< 0.1	< 0.1
50-90	0	< 0.1	< 0.1	0	0	0

[a] mean ± standard error

Leaching of ^{14}C. At 1 - 12 MAA, an average of 89 % of the ^{14}C present in the soil column was in the top 10 cm (Table II). However, between application and 1 MAA, ^{14}C leached to the 90-cm depth, but was < 0.1 % of applied. Macroporous flow through the soil appears responsible for this rapid movement of ^{14}C during the first MAA. During this time only 2.3 cm of rainfall was received as four separate events of less than 0.8 cm and 2.5 cm of irrigation water was applied as a ponded application. Therefore, sufficient water was not available to move the ^{14}C residues 70 to 90 cm unless macroporous flow occurred. Movement of ^{14}C to the bottom of the columns without appearance of ^{14}C or water in the glass block water samplers also suggests that macroporous water flow, and not piston-type flow, was responsible for the rapid movement of ^{14}C residues through soil. As columns were sectioned, macropores were observed to be continuous from the base of the column to the soil surface. Because the pores were vertical and approximately 6-mm diam, they appear to have been made by nightcrawlers (*Lumbricus terrestris*)

While most of the ^{14}C remained in the surface soil, significant amounts of ^{14}C (3.3 to 8.4%) were found at the 10 to 20 cm depth. The maximum amount of ^{14}C found at depths > 20 cm was 2.0 % of applied at 12 MAA, and the maximum at > 40 cm was 0.5 % at 1 MAA. No ^{14}C was detected in soil below 50-cm depth from 6 to 16 MAA. No ^{14}C was also detected in water collected in the glass blocks following spring recharge, which occurred between 6 and 12 MAA.

Degradation. The ^{14}C residues detected and confirmed in the top 10 cm of soil were dicamba and 3,6-DCSA. The amounts of ^{14}C in the subsurface soil were too low for confirmation of any chemical. The metabolite 5-HO-dicamba, which we could not confirm, probably originated from oxidation of dicamba during the extraction process.

Dicamba degradation was rapid, only 5.5 % of applied ^{14}C remaining at 1 MAA was dicamba (Table III). From 2 to 16 MAA, recovered ^{14}C with a HPLC retention time corresponding to dicamba, comprised 1 - 2% of applied ^{14}C (equivalent to < 20 ng g^{-1}), but its identity could not be confirmed. These data raise the question as to whether small amounts of dicamba could have diffused into small

Table III. Product distribution of extractable ^{14}C in the top 10 cm of soil.

Chemical	Months after application					
	0	1	2	6	12	16
	% of applied ^{14}C[a]					
dicamba	95.6	5.5	2.2?[b]	1.7?	1.4?	1.0?
3,6-DCSA	3.4?	26.7	15.2	11.0	12.9	9.4
5-HO-dicamba	0.4?	0.2?	0.2?	0.2?	0.2?	0.1?
nonpolar	0.1	0.2	0.2	0.2	0.2	0.2
polar	0.4	2.3	2.4	2.0	2.1	0.2
unextractable	0	58.2	36.2	38.8	30.3	31.8

[a] average coefficient of variation over sampling times: dicamba = 9.0%; 3,6-DCSA = 6.4 %; unextractable = 8.0%.

[b] ? indicates that identity of the ^{14}C could not be confirmed.

soil pores where it was protected against degradation, or we just observed a recalcitrant unknown metabolite that coeluted on the HPLC with dicamba.

The major metabolite identified was 3,6-DCSA. The amount of 3,6-DCSA in the top 10 cm of soil was a maximum 26.7 % at 1 MAA, corresponding to the rapid degradation of dicamba. 3,6-DCSA then slowly degraded to an average of 13.1 % at 2 to 6 MAA and an average 11.2 % at 12 to 16 MAA. The amount of total unidentified polar and nonpolar ranged from 2.2 to 5.6 during the 16 months. The greatest amount of unextractable ^{14}C was 58.2 % at 1 MAA corresponding to the period of rapid dicamba degradation. It then decreased to 31.8 % at 16 MAA, indicating that the bound residues were slowly available for mineralization.

In summary, use of ^{14}C-pesticides in large intact field lysimeters is an effective method for elucidation of mechanisms and processes controlling pesticide fate in soil. For instance, in this study we showed that rapid degradation and formation of bound residues allayed leaching of dicamba despite it very low sorption potential. By using ^{14}C-pesticides in large intact field lysimeters, we were also able to show that the major metabolites remained in the top 20 cm of soil. Trace quantities of ^{14}C did leach to a depth of 90 cm as the result of macroporous flow. However, because of the low amounts, we were not able to positively identify the ^{14}C-labeled chemicals.

Acknowledgments.

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Chapter 9

Demonstration of the Functionality of a Self-Contained Modular Lysimeter Design for Studying the Fate and Transport of Chemicals in Soil Under Field Conditions

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Analytical Bio-Chemistry (ABC) Laboratories, Inc. has developed a modular lysimeter design and has instrumented and installed the lysimeters at four field sites in the United States: Missouri (MO), Iowa (IA), Illinois (IL), North Carolina (NC) and Ontario (ON), Canada. The modular lysimeter design consists of three components that are readily assembled and installed in the field; an intact soil core, a run-off (overflow) collection system, and a leachate collection system. In NC, the lysimeters were installed at the NC State University Experimental Station site in Clayton with a Novartis Crop Protection development compound, designated as ^{14}C-XYZ for confidentiality reasons. The fate and transport of the chemical was studied over a period of 90 days using intact 90 cm deep, 15 cm diameter soil columns containing sandy soil. Parent compound degraded into an acid metabolite that was detected down to 60 cm in the soil profile. Parent compound was not observed at a soil depth below 15 cm. The decline of the parent compound coincided with the formation of the acid metabolite which degraded into four additional metabolites. Lysimeters 30 cm in diameter and 75-90 cm deep were instrumented and installed at four locations (MO, IA, IL, and ON) to study the fate and transport of a DowElanco development compound, designated as ^{14}C-DEC for confidentiality reasons. In these experiments, the fate and transport of the test compound and a bromide tracer in the lysimeters were compared with that in the field plots for 12 months. Preliminary results from IA and MO suggest that degradation and solute transport processes were similar in the soil plots and lysimeters, and that the 30 cm diameter pipe lysimeters approach the representative elementary volume (REV) for solute transport processes at the IA site. The modular pipe lysimeter design offers significant advantages in terms of assessing solute mass balance, mobility, variability (through increased replication) and reduced cost of radioactive waste compared to soil plot studies.

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Evaluating the degradation, adsorption, run-off (overflow), and leaching of chemicals in soil under actual field conditions is important in predicting their movement to surface and ground water. Soil, surface water, and ground water are potential recipients of chemical contaminants and are the environmental matrices of concern from environmental and human health perspectives. Assessment of risk to the terrestrial and aquatic organisms and to humans often involves the use of data generated from *in-situ* field experiments and predictive modeling. Lysimeters have been used extensively for assessing the environmental fate and mobility of agricultural chemicals, and their use has been reviewed in detail by Winton and Weber (1996). The lysimeter design developed by ABC Laboratories, Inc. provides an opportunity to study the fate and transport of chemicals and to generate reliable data on degradation, adsorption, run-off (overflow), leaching, and surface overflow (run-off) of chemicals applied to soils. These data are useful in prediction of risks of chemicals to human and environmental health.

Materials and Methods

The Modular Experimental Design. The modular ABC lysimeter design (U.S. Patent No. #5,594,185) incorporates a soil column, a leachate collection component, and a run-off collection component. All three modules are assembled in the field and placed in the ground in direct contact with the surrounding soil, thus maintaining an *in-situ* field moisture, % humidity, and temperature profile. The run-off/overflow component of the design is to preserve mass balance, i.e. to keep radioactivity from running over the top edge of the column in the event of excessive rainfall. The self-contained nature of these components enables conduct of studies using radiolabeled test substances without risk of contaminating the surrounding soil (Figure 1). The modular design can be adapted to field sites with varying climatic conditions. For example, in lysimeters installed in Ontario (ON), Canada, the soil core was anchored to concrete support pillars for stability during freezing winters, since the frost line in this area is deeper than the length of the soil column (Figure 2).

Experiments Conducted in North Carolina. The degradation and mobility of the Novartis compound, XYZ, and its degradation products was monitored under field conditions in Clayton, North Carolina (NC) using outdoor lysimeters. The control soil in the intact soil core was segmented and was characterized as a sandy loam transitioning to loamy sand with increasing depth. pH ranged from 5.0 to 6.3 and organic matter from 0.4 to 2.6% with increasing depth.

Collection of Soil Cores, Instrumentation and Installation of Lysimeter. The 15 cm steel pipes were obtained commercially pre-cut to 100 cm in length. Steel hooks were welded to the steel pipes to facilitate installation of the lysimeters in the ground or their removal from the ground. The leachate and run-off (surface overflow) collection systems consisted of commercially available PVC pipes capped at one end.

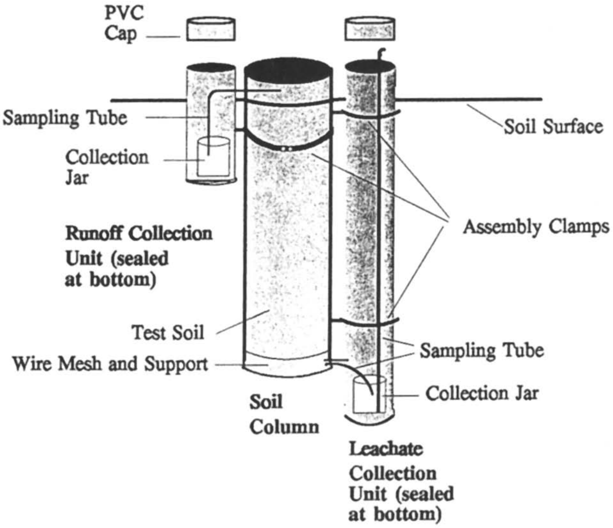
PVC Cap
Sampling Tube
Collection Jar
Runoff Collection Unit (sealed at bottom)
Test Soil
Wire Mesh and Support
Soil Column
Soil Surface
Assembly Clamps
Sampling Tube
Collection Jar
Leachate Collection Unit (sealed at bottom)

Figure 1. A Graphic Representation of Design Used at the North Carolina Field Site.

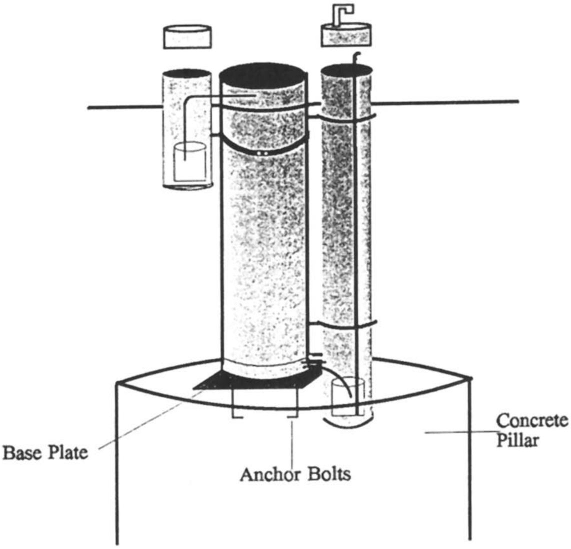
Base Plate
Anchor Bolts
Concrete Pillar

Figure 2. A Graphic Representation of Design Used at Field Sites in Missouri, Iowa, Illinois, and Canada. The concrete pillar as a base support was only used in Canada.

This collection system was connected to the soil column via teflon tubing between corresponding holes in the soil column and leachate component. Similarly, the leachate collection system was connected to the base of the soil column via teflon tubing between two sets of corresponding holes in the soil column. The leachate and run-off collection systems were fitted with an appropriate size PVC cap to prevent entry of direct rainfall. Intact soil cores were collected from the Agricultural Experimental Station of North Carolina State University in Clayton, NC by pressing a 100 cm long and 15 cm diameter steel pipe into the ground using a backhoe. Core integrity was monitored by visually examining the soil compaction (< 5 cm acceptable), as well as leaching of water through selected soil cores prior to treatment with the test substance. The pipes containing soil cores were subsequently lifted from soil. Approximately 10 cm of the soil was removed from the bottom of the intact soil core, creating the leachate collection area and freeing the two holes designated for the leachate collection system. A wire mesh held in place by a metal tripod was placed at the bottom of the core to support the soil column. The bottom of the soil core (leachate collection area) was sealed with an aluminum flashing tightly banded and caulked to the bottom of the soil core. The soil core was then instrumented with the run-off and leachate collection systems. The run-off and leachate collection modules contained a silanized glass vessel to collect run-off or leachate as it was produced. A teflon tube was placed in the silanized glass vessel and ran down the length of the leachate collection module for leachate sampling. The lysimeter clusters were buried in the soil back to soil surface level and allowed to acclimate to the surrounding environment for approximately three weeks before application of the test substance. Seven XYZ-treated lysimeters and one untreated control lysimeter were used for the study.

Over the duration of the study, daily rainfall amounts, air and soil temperatures, and pan evaporation were obtained from the nearest National Oceanographic and Atmospheric Association (NOAA) recording station in Raleigh, NC. Rainfall during the test period was 135% of the 10-year average amount of rainfall.

Application of Test Substance. The surface of each soil core was dosed at a nominal concentration of 3.65 kg ai/ha (3 lbs ai/A) of the radiolabeled test substance (specific activity = 12.3 μCi/mg). The dose solution was prepared by dissolving 55.2 mg of XYZ in 4 mL of acetonitrile:acidified water (8:2, v:v). Approximately 0.45 mL of dose solution in acetonitrile:acidified water (8:2, v:v) containing ~9.7 μCi/mg (4,500 dpm/g) of radioactivity was applied to each lysimeter in a manner to ensure even coverage to the exposed surface of the intact soil core of each of the seven treated lysimeters. An irrigation volume of ~30 mL of de-ionized (DI) water was added to each treated lysimeter immediately following application.

Sampling and Analysis. Visual observations of leachate and surface overflow were made on a weekly basis or after heavy rainfall, and leachate and surface overflow were collected when present. Leachates were collected by attaching a pipetter vacuum pump to the end of the sampling tubes and withdrawing entire leachate into a silylated amber sample bottle. The sample bottle was removed, capped, labeled, and shipped frozen to ABC Laboratories for radioassay and component analysis. Surface overflow collection bottles were accessed by hand and shipped in the same manner.

A single treated lysimeter was removed randomly from the field at day 0, 1 ,3, 14, 30, 62, and 90 following the application of the test substance. The control lysimeter was taken at day 90. The leachate and run-off/overflow units were disassembled from the soil core unit in the field. The intact soil cores were capped at both ends and immediately placed in a cooler with dry ice and shipped to ABC Laboratories. After they were received and logged at ABC Laboratories, the soil cores were stored frozen (-20°C) until analysis. The frozen soil cores were sectioned into 0-7.5, 7.5-15, 15-30, 30-45, 45-60, 60-75 and 75-90 cm segments with a power saw.

Soils from each segment were homogenized and ground with dry ice. Following at least 24 hours of freezer storage to remove the dry ice, the total mass of the homogenized soil in each segment was determined. Nine aliquots (~500 mg wet weight basis) of each soil were combusted to determine the total amount of ^{14}C-residues in each soil segment. Soil segments containing or approaching 10% of the applied radioactivity were extracted and analyzed by HPLC to determine the concentration of the parent compound and its degradation products.

Experiments Conducted in Missouri and Iowa. The degradation and the mobility of two labels of the DowElanco ^{14}C-DEC test compound was compared between lysimeters and field plots at two locations; one located on a silty loam overlying a silty clay loam soil [pH=6, Organic Matter (OM)=2.5%] at the ABC Laboratories site in Columbia, Missouri (MO), and the other located on a loam overlying a sandy loam/loamy sand (pH=6.5, OM=3%) soil in Cedar Falls, Iowa (IA). At each site two-1 m x 5 m bordered plots were instrumented with run-off/overflow collection systems and were treated with one of the two labeled test materials. An untreated control plot (2.4 m x 3 m) was located approximately 5 m upwind from the treated plots and was treated with potassium bromide (KBr) tracer. Nine 30 cm diameter steel pipe lysimeters were installed adjacent to the soil plots to a depth of 90 cm at each site. The lysimeters were installed in the fall, approximately six months prior to application to allow acclimation to the surrounding soil environment. Eight lysimeters were treated with the test compound (4 with each label) and with the bromide tracer. One control lysimeter was treated with bromide only. Analysis of the DowElanco test compound is currently in progress, thus only a description of the bromide tracer mobility is described in this manuscript.

Collection of Soil Cores, Instrumentation and Installation of Lysimeters. The 30 cm diameter, 100 cm deep steel pipes used to collect the intact soil core were obtained pre-cut from a commercial supplier in Columbia, MO. Steel hooks were welded to the top of the lysimeter to facilitate installation or removal of steel pipes into and from soil, respectively. The run-off/overflow collection component was a metal canister open at the top end and sealed at the bottom. The runoff/overflow collection modules were tightly banded to the soil column with metal clamps to prevent movement during freeze and thaw. The leachate collection component was a PVC pipe capped at the bottom with a glass collection jar. The run-off/overflow collection system was connected to the soil column via teflon tubing between corresponding holes in the soil column and run-off/overflow component. Similarly, the leachate collection system was connected to the base of the soil column via teflon tubing between two sets of corresponding holes in the soil column and leachate component. The leachate and run-off components were fitted with PVC caps of appropriate dimension in order to prevent rain water from directly entering (Figure 2). The cap of the leachate component was fitted with U-shaped vent tube to ensure that an atmospheric pressure boundary condition was maintained at the bottom of the lysimeter. The collection of soil cores and installation of the lysimeters was similar to that described for North Carolina.

Plot Preparation and Maintenance. The plant cover in the control plot and lysimeters was removed prior to the bromide tracer application and was maintained under bare soil condition for the duration of the study. Weeds growing in the plots and lysimeters were removed after application by cutting them at the soil surface and placing the back into the plot.

Climatological data. An automated weather station was installed at both test sites. The weather station recorded precipitation (rain and snow), air temperature, soil temperature (2.5, 10, 50 cm), wind speed and direction and solar irradiance. A Time Domain Reflectometry (TDR) system was installed in the control plot at each site to monitor volumetric soil water content at the 15, 30, 45, 60 and 90 cm depths.

Irrigation. Irrigation was applied to the plots and lysimeters during the growing season to ensure that total precipitation plus irrigation amounted to at least 125% of the 30 year monthly average rainfall amounts reported by the nearest NOAA site. Irrigation rate was not allowed to exceed the infiltration rate to prevent ponding. In the field plot irrigation amounts were measured by the use of rain gauges placed at various points on the plot. The lysimeters were irrigated separately using a perforated container that covered the surface area of the lysimeter and allowed irrigation water to drip uniformly across the soil surface.

Application of the Bromide Tracer. KBr was broadcast sprayed on the control plot and treated lysimeters at a rate of 150 kg/ha (15 g/m^2), after the test substance had been applied. Approximately 5 mm of water was added to the plots and lysimeters after application of the test substance and the KBr.

Sampling and Analysis for Bromide Tracer. Cores for bromide analysis were taken from the field plots on day 0, and 2, 4, 10 and 21 weeks after treatment (WAT). Samples were taken at 0-15 cm depth only on day 0. For subsequent intervals cores for bromide analysis were taken from 0-90 cm using a 3 stage probe with diameters of 7.5, 5, and 2.5 cm respectively for the 0-15, 15-45, and 45-90 cm stage. As each stage was completed, a steel casing remained in the hole to prevent contamination of deeper depths. Soil cores for bromide analysis were sectioned every six inches and composited by ABC Laboratories before being shipped to DowElanco. Soil cores were also taken from two of the lysimeters at 14 WAT and from the 6 remaining lysimeters at the termination of the study (52 WAT) and shipped to DowElanco for analysis of the bromide tracer. Run-off/overflow and leachate were collected from the lysimeters weekly, or after significant run-off/overflow or leaching events. Soil, leachate, and run-off/overflow samples were frozen and shipped to DowElanco for the test substance and bromide tracer analysis. For the Br^- analysis, soil samples from the field were weighed, mixed, and a 5 g subsample was extracted using 20 mL of DI water. Soil extracts and leachate water were analyzed for bromide concentration using a bromide specific electrode with a limit of detection (LOD) of 0.3 ppm.

Modeling of Bromide Leaching. The pesticide leaching model (PLM) incorporates the pesticide adsorption and degradation routines from the CALF model (Walker and Barnes, 1981; Nicholls, Walker and Baker, 1982) into the solute leaching model (SLM; Hall, 1993). PLM divides the soil profile into 5 cm layers between which soil solution is exchanged to simulate internal drainage and soil drying by evaporation. Soil solution is partitioned into mobile and immobile components, within each layer, with only the mobile components being displaced during drainage. Solute is permitted to diffuse between the two components. The program operates on a daily time step and is driven by the inputs of rainfall, evapotranspiration and maximum and minimum air temperatures.

Since most soils drain rapidly to field capacity which has been defined by a matric potential of -5 kPa (Webster and Beckett, 1972), the volume of pores available for mobile water is estimated to be equal to the volume of pores air filled at -5 kPa potential. The volume of pores available to the immobile component is equal to the volume of pores water-filled at the same potential. The mobile phase is sub-divided into "fast" and "slow" domains which are empirically determined for the soils tested. Essentially this becomes a calibration factor for predicting hydrology for a particular site. Additional details of the model can be obtained from the PLM user's manual.

For the IA study, actual soil and weather data at the site were available as model inputs. Initial runs were conducted and compared to the bromide leaching data in order to obtain (calibrate) the relative proportions of the "fast" and "slow" mobile phase. Once the model was calibrated for the bromide data, and therefore adequately describing the site hydrology, it can be used to predict test substance movement.

Results and Discussion

North Carolina Site.

Mobility of the Test Substance. Movement of the radioactivity through the soil core was observed with time. However, the vast majority of the radioactivity was found in the top 30 cm. Radioactivity was also detected in the 30-45 cm and 45-60 cm segments during the course of the study, but did not exceed 5% of the applied dose. No radioactivity above the minimum quantifiable limit (MQL) was observed in the 60-75 cm or 75-90 cm segments during the course of the study (Figure 3). Radioactivity was detected in the leachate only at a few sampling times. The highest amount of radioactivity observed in the leachate was 0.014% of the applied dose at day 30 sampling. Minor amounts of radioactivity were also observed in the surface overflow samples in the day 60 and 90 samplings. The amount of radioactivity in the run-off/overflow never exceeded 0.01% of the applied dose at any single event. The approximate MQL in soil by combustion radioanalysis was 2×10^{-3} mg/kg (ppm) while the MQL in the leachate and overflow was 7.5×10^{-4} mg/mL. The difference in MQL between soil and water justifies the presence of ^{14}C-activity in the leachate with no radioactivity observed in the lower soil core segments at specific sampling times.

Degradation and Depletion of the Test Substance. The parent compound decreased rapidly during the first 30 days of the study ranging from 102.9% of the applied dose at day 0 to 16.3% of the applied dose at day 30. The amount of the parent compound at study termination (90 days) was 16.4% of the applied activity and was primarily observed in the 0-7.5 cm segment. Only minor amounts of the parent compound were observed in the segments below 7.5 cm (<5% of the applied dose). Six degradation products were observed during the HPLC analysis of the soil extracts. The only degradate exceeding 10% of the applied dose was a more polar acid metabolite. The amount of this degradate increased rapidly during the course of the study and reached a high of 53.2% of the applied dose at day 14, and declined slightly after day 14 and was 42.5% of the applied dose at study termination (day 90). The acid metabolite was the primary component observed in the soil segments analyzed below 15 cm with the highest total amount of 53.2% at day 14. No radioactivity was detected at 60-100 m depth. The amount of all other degradation products combined did not exceed 7% in any of the soil segments (Figure 4). The degradation rate of ^{14}C-XYZ, based on the entire column, was bi-phasic. The log-linear regression curves are depicted in Figure 5.

No contamination of soil under the lysimeter modules or around the lysimeter modules occurred during the course of the study since radioactivity was less than twice the soil background radioactivity as observed from the data on combustion of the soil samples collected under and around lysimeters.

Iowa and Missouri Sites. Despite the application of 125% of normal rainfall at the MO site, no leachate occurred during the study, however, significant runoff/overflow volumes were collected due to the heavier soil texture at the site. The silty clay soil

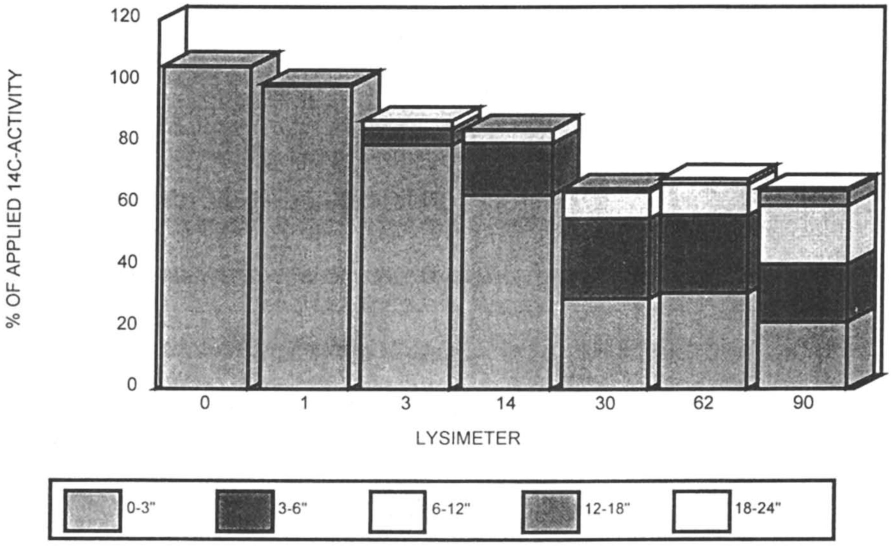

Figure 3. Radioactivity Distribution Throughout Soil Profile at time 0 and 1, 2, 3, 14, 30, 62, and 90 days after treatment - North Carolina Experiment.

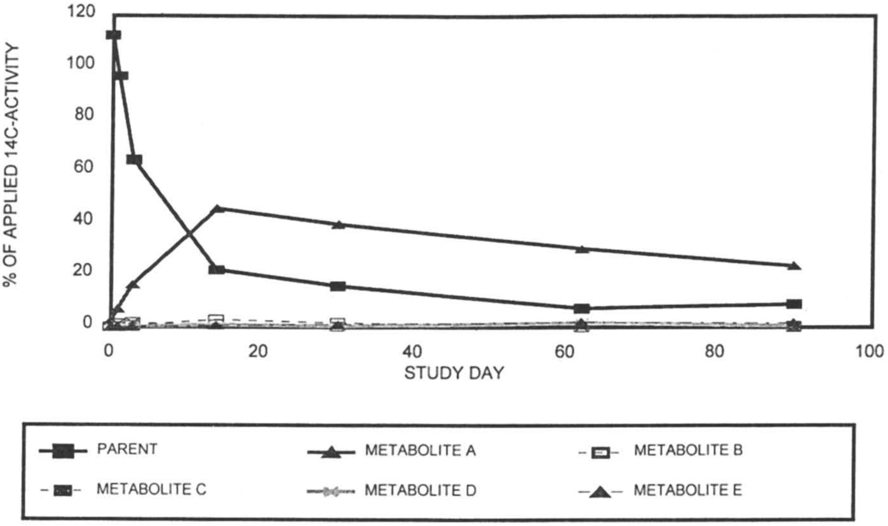

Figure 4. Decline of the Parent and Formation and Decline of Degradates - North Carolina Experiment.

and the clay pan originating at approximately 50 cm prevented any downward movement and resulted in no leachate flow downward. The runoff/overflow data are being analyzed. Subsequent description of the data in this section relates only to the Iowa site. The leachate data for Iowa are reported here.

Leachate Data. Figure 6 shows the average volume of leachate and bromide concentration observed from the lysimeter at the IA site. The coefficients of variation (CV's) for leachate volume and bromide concentration (average CV for all leaching events=30%) are low compared to the typical degree of variability encountered in the field for soil hydraulic properties controlling flow processes such as hydraulic conductivity which can exceed CV's of 150% (van Wesenbeeck and Kachanoski, 1995). The low CV's indicate that water flow and bromide movement were relatively uniform through the 8 lysimeters and indicate that these 30 cm diameter lysimeters are approaching the representative elementary volume (REV) for solute transport for this soil. Thus, the average of 6-8 lysimeters of these dimensions in this soil should adequately represent field average leaching behavior. Bromide tracer did not appear in significant quantities in the leachate until approximately 70 DAT. Bromide concentrations then followed classic breakthrough behaviour for a conservative, non-reactive tracer, increasing to a peak at approximately 120 DAT and then decreasing until soil freeze-up which occurred at approximately 155 DAT (November 7, 1996). Soil remained frozen until approximately 270 DAT (March 4, 1997), when flow resumed and bromide concentrations continued to decrease. Approximately 60% of the bromide had leached through the lysimeters during the first growing season prior to freeze-up. Analysis of leachate from DAT 290 to 365 is underway.

Hydrology. Figure 7 shows the excellent agreement between the observed cumulative volume of water leached and the PLM predicted volumes. PLM predicted leachate volumes were within 2L of the mean observed values (n=8) for each sampling event. The only factors that were adjusted to obtain this fit to the observed data were the evaporation factor and the initial water deficit.

Bromide Leaching. PLM was executed using a $K_d = 0$ and $T_{1/2} = 0$ (for non-reactive, conservative tracer) to simulate the leaching of bromide through the soil profile. The "% of fast flow" factor was varied from 20% to 82%, with 75% being the optimum value for predicting both the timing and cumulative mass of bromide leaching out of the lysimeter. Figure 7 shows the remarkable agreement between the observed (average of 8 lysimeters) and predicted bromide leaching for the first 146 days of the study. Clearly the model is adequately predicting both the magnitude and the time of arrival of the bulk of the bromide tracer in the lysimeter leachate. The model slightly under-predicted the leading edge of the bromide tracer.

The agreement between the model and the observed data suggests that the bromide leaching is behaving in a predictable pattern in the lysimeter system based on weather and soil properties at the site. The use of the 75 % "fast flow" factor in the model to optimize the fit to the data suggests that there is a portion of the flow

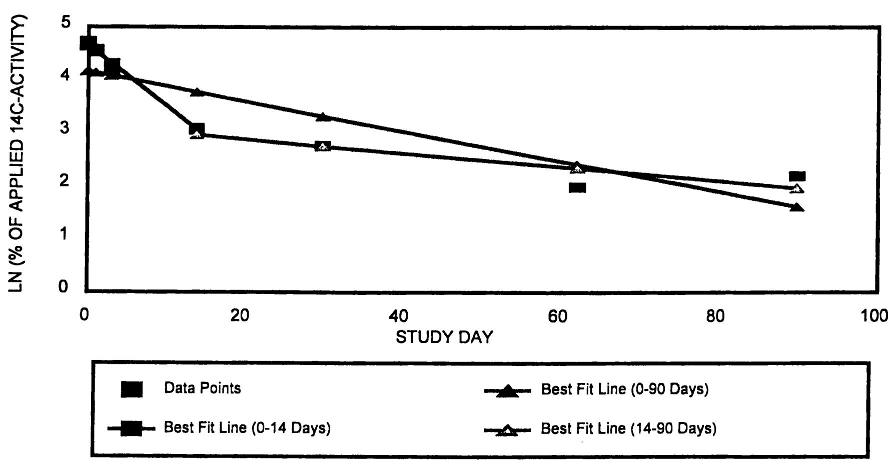

Figure 5. Half-Life Determination for the Degradation of the Parent - North Carolina Experiment.

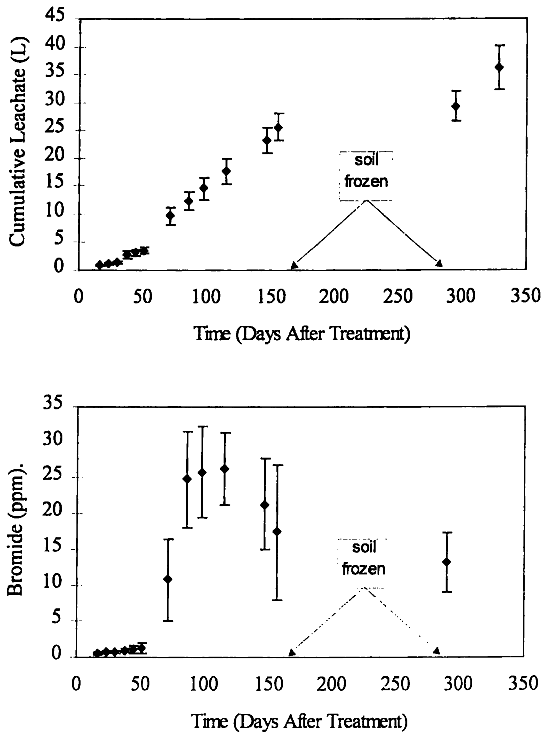

Figure 6. Average cumulative leachate volume (top) and average bromide concentration (bottom) at the Iowa site for 8 lysimeters. Error bars represent +/- one standard deviation from the mean.

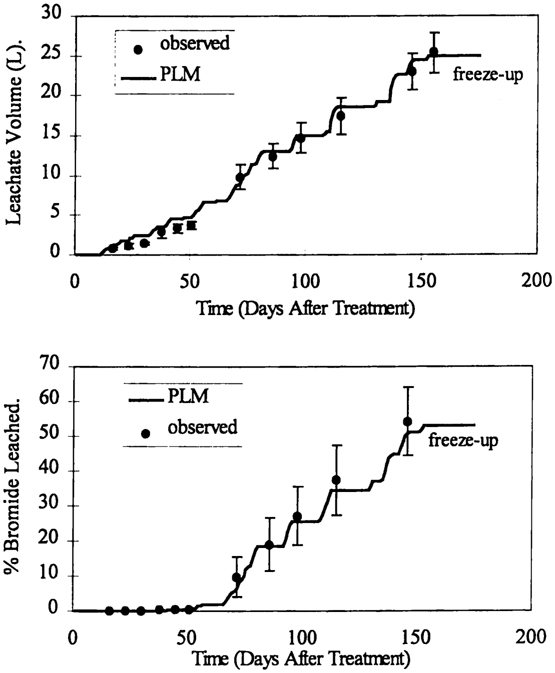

Figure 7. Average cumulative leachate volume (top) and average % bromide leached (bottom) compared to PLM predictions at the Iowa site for 8 lysimeters. Error bars represent +/- one standard deviation from the mean.

that is moving through macropores and not as matrix flow. Examination of the lysimeters during instrumentation revealed that there were old root channels and worm holes at the bottom of the lysimeters which could act as channels for preferential flow of water and solute. No cracks or gaps were visible at the soil/lysimeter interface during installation or at the end of the study when the lysimeters were disassembled.

Comparison of soil plots and lysimeters. Preliminary analysis of the DowElanco test compound from a set of lysimeters sampled at 14 WAT indicates that both degradation kinetics and distribution of the test material and metabolites in the soil profile were similar to that found in the soil plots at 14 WAT. This suggests that lysimeters can be a useful replacement for a traditional soil dissipation study in situations where information on the mobility of the test compound is required in addition to field degradation behaviour. Kubiak et.al (1988) and others have shown that soil moisture and temperature profiles and subsequent pesticide residue distribution in soil and leachate were similar for lysimeters and soil plots.

Future Work. Modeling the mobility and degradation of the DowElanco test compound using the PLM model calibrated on the bromide data will be conducted. A comparison of the predictive capabilities of the PLM model and the PRZM model for this data set will also be made. The study will include further comparison of the behaviour of the test compound in the soil plots and lysimeters at additional time points.

Conclusions. The lysimeter design patented by ABC Laboratories has been shown to be an effective tool for a realistic determination of degradation and mobility of test chemicals *in-situ* in intact soil cores. The modular design incorporates a self-contained soil column and leachate and run-off/overflow collection components which prevent contamination of the test site with radiolabeled test substances. In the ABC lysimeter design, soil core, leachate, and run-off/overflow collection modules are completely surrounded by soil, thus maintaining an *in-situ* temperature profile. The modular design can be adapted to field sites with varying climatic conditions. For example, for installation at the Ontario, Canada site the soil core was attached to concrete support pillars for additional stability since the frost line in this area is deeper than the length of the soil column. The components of this system permit flexibility in soil core dimensions and core casing materials which allow for minimal test substance adsorption, minimal compaction during soil core generation, and maximum strength for introduction into heavy clay soils.

In field tests conducted in NC, MO, and IA, the versatility and functionality of the modular ABC lysimeter design for collection of leachate and run-off/overflow for determining the mobility of the test chemical within the soil core was demonstrated. The decline of parent compound, formation and decline of the degradates, and the radioactivity in leachate and surface overflow was monitored in lysimeters installed at these sites.

At the MO and IA sites, the quantity of contaminated soil requiring incineration was significantly greater from the soil plots than from the lysimeters, resulting in significant cost savings. The containment of radioactivity within the modules was demonstrated when no radioactivity above background was observed in soils collected from under the lysimeter units or in the surrounding soil at the conclusion of the experiments at all three field sites (NC, MO, and IA) where ^{14}C-radiolabeled materials were used.

The lysimeter allows accountability of radioactivity in leachate, surface overflow, and soil core as well as simultaneous assessment of degradation and mobility. The total mass of applied material lost through leaching can be estimated more precisely using pipe lysimeters than using porous cup lysimeters or direct soil measurement, since the exact volume of flow, as well as the concentration, is measured for each leaching event. When porous cup lysimeters are used, estimation of total mass lost due to leaching requires estimation of the flow field which is difficult and prone to significant uncertainty. Additionally, pipe lysimeters account for all the flow occurring within the system and thus preclude the possibility of missing an entire leaching event as is possible when using porous cup lysimeters. The pipe lysimeter design also allows a greater degree of replication and assessment of variability compared to studies incorporating either soil plots or large soil monoliths.

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Chapter 10

The Movement of ^{14}C-Benazolin and Bromide in Large Zero-Tension Outdoor Lysimeters and the Undisturbed Field

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The leaching behavior of ^{14}C-labeled benazolin and bromide in suction-free lysimeters of 0.8 m^2 surface area was compared with a suction base system of the same size that was very close to the undisturbed field. Differences were found in the outflow of leachate and bromide which could be explained by the different climatic boundary conditions at the two experimental sites. The outflow of ^{14}C-activity and benazolin was almost identical with the two systems, whereas large variabilities in the replicates were found within the systems. Parts of the herbicide and the conservative tracer simultaneously reached the sampling depth in 1.3 m. No differences were found between the bromide transport of the undisturbed field and the suction plots.

In order to assess the leaching behavior of pesticides, large undisturbed lysimeters are used to obtain the link between perfectly controlled laboratory experiments, and the natural conditions with realistic scenarios of field experiments. In contrast to field studies, lysimeters allow the use of ^{14}C-labeled pesticides which provide many additional possibilities (*1*). In field studies, where only a subset of the entire field is sampled, fast solute leaching through a small proportion of the soil matrix will rarely be detected. However, regarding leaching experiments, in lysimeters all solutes which reach and pass through the bottom of the soil cores were detected, and therefore preferential flow of solutes can be clearly identified.

Nevertheless, several differences between zero-tension lysimeters and the actual field situation exist: First, at the lower boundary of the lysimeters there is a soil-atmosphere interface, and zero-tension or higher matric potential is permanently adjusted during the drainage period. Due to that capillary barrier, a capillary fringe will be found, which influences soil water and solute dynamics. Secondly, the lysimeter wall prevents lateral water and solute flux out of the defined soil core, and therefore no horizontal dispersion of the solute pulse applied is possible. Finally, the

In The Lysimeter Concept; Führ, F., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 1998.

collection and the transport of the lysimeter cores may induce disturbances of the soil structure which may cause fissures or macro-pores within the soil core. These artificial flow channels may function as preferential flow paths for solutes. Cracks may also exist between the lysimeter wall and the soil core.

Due to the decisive character of lysimeter studies for the pesticide registration in some countries (*2*), knowledge about the validity of the results and their transferability to the actual field situation is of great importance. Kubiak et al. (*3*) found no significant differences between the metabolism and translocation of metamitron in lysimeters and the undisturbed field. However, their sampling strategy did not provide for the detection of preferential flow events.

In the present study, the leaching behavior of ^{14}C-benazolin which served as a model herbicide should be compared under lysimeter and field conditions. Therefore, a sampling device in the field had to be developed which provided an adequate sampling technique for drainage water at a cross-sectional area as with a lysimeter. Simultaneously, the intact soil system should not be affected and the natural flow conditions for soil water and solutes have to be maintained.

A field leaching experiment with a conservative tracer was additionally initiated to evaluate the function of the field sampling device. Therefore, the bromide sampled in the leachate of the sampling devices (bromide that moved deeper than 1.3 m) had to be compared to the bromide found within the soil profile of the completely undisturbed field.

Materials and Methods

Soil and Location. The soil that was used for all studies of this project was collected from a field site close to the village of Birkenheide (Rhineland-Palatinate) in South-Western Germany. At this site the field research station with the grid suction units was installed and the lysimeters were taken. The field was about 20 km away from the lysimeter station.

Table I: Properties of the Birkenheide soil.

Depth	pH	Biomass†	C_{org}	Sand	Silt	Clay	ρ_r
- cm -		mg kg^{-1}		%			kg L^{-1}
0 -30	5.9	85 - 570	0.45 - 0.70	69.8	22.5	7.7	1.48
30 - 70	5.5	25 - 30	0.12 - 0.15	71.3	21.9	6.8	1.58
70 - 100	6.0	30 - 40	0.14 - 0.19	70.1	19.8	10.1	1.72
100 - 130	7.9	50 - 70	0.09 - 0.18	72.2	22.4	5.4	1.80

† Substrate induced respiration (SIR)

According to the FAO-classification of soils the Birkenheide Soil is a Luvic Arenosol developed from aeolian sand over fluvial loams. Three predominant soil layers down to 1.3 m are visible. The upper 25 - 30 cm are characterized by a well mixed Ap-horizon with a firm structure. It is followed by a 50 cm (±10) deep poorly structured Btw-horizon. The third layer shows a coherent to subangular blocky structure. Additional information can be taken from Table I.

Chemicals and Analysis

Bromide. Due to its conservative behavior in natural field soils and its small natural occurrence (*4*), bromide was selected as a water tracer. It was applied as sodium bromide.

For analysis, leachate with bromide was filtered with 0.45 µm filters (Millipore HV) and after that, directly injected into the HPLC. Soil samples were first air-dried and then passed through a 2 mm sieve, and extracted with distilled water at a soil-water ratio of 1:1. After centrifugation, 2 mL of the supernatant were decanted and filtered.

The samples were analyzed with a HPLC fitted with an anion column (Dionex, Ion Pak AG4A 4mm) with precolumn and a conductivity detector (Pharmacia).

Benazolin. Benazolin (4-chloro-2-oxobenothiazolin-3-ylacetic acid) is a selective, systemic, growth-regulator, post-emergence herbicide. The physico-chemical properties are shown in Table II. Benazolin is the corresponding acid and the first transformation product of benazolin-ethyl that disappears in soils by de-esterification with a half life time (DT_{50} of approx. 1-2 days (*5*).

Table II: Physico-chemical properties of benazolin

Properties		
Molecular weight	243.7	g mol^{-1}
Melting point	193	°C
Vapor pressure	100	nPa (20 °C)
K_{ow} logP	1.34	(20 °C, pH 7)
Aqueous solubility	500	mg L^{-1}
pKa	3.04	(20 °C)

Benazolin was applied as Galtak® (Agrevo) in which ^{14}C-benazolin-ethyl was formulated as an emulsifiable concentrate (ec). Galtak® contains 89.7 g benazolin-ethyl per liter and was used at the maximum recommended application rate of 448.5 g ha^{-1} at a dose of approx. 1 g L^{-1}. To the lysimeter and the suction plots, benazolin-ethyl was applied in a radiolabeled form with a specific ^{14}C-activity of 1.98 MBq mg^{-1}.

The ^{14}C-activity of the collected leachates was measured with a liquid scintillation counter (LSC, 2550 TR/LL Canberra Packard). The proportion of the ^{14}C-labeled metabolites was investigated by chromatographical analysis with radio-TLC as well as radio-HPLC. Therefore, the ^{14}C-labeled metabolites were extracted from the leachate by solid-phase-extraction with a C_{18} reversed phase column (1000 mg, Macharey and Nagel).

The Suction-Free Lysimeters. For the present study three lysimeters were used, which will be denoted as MRL I-III (Mussbach **Regulatory** Lysimeter). The lysimeter vessels were made of stainless steel with 1 m i.d. and 1.3 m height. A thin wire netting and a bottom plate with 72 boreholes (1.5 cm i.d.) were attached to the lower end of the cores to keep the soil within the container and provide for free leachate outflow (*6*).

In order to record the change in the average volumetric water content of the soil cores ($\Delta\theta_{average}$), the lysimeters were equipped with a special weighing device (Mettler Toledo).

The three cores were collected about one and a half years prior to the application of the chemicals. A large excavator pressed the steel cylinders into the field soil and carefully lifted them out again. The field soil broke at the lysimeter base, resulting in a nearly smooth soil surface at the lower soil core end. This technique kept the soil in its original state and prevented a smearing and closing of the pores at the lower column end.

The Field Station with the Grid Suction Bases

The Measuring Tunnel. A field research station was built at the Birkenheide field site, 5-10 m beside the location from which the lysimeters were collected. A trench, 10 m long, 3 m wide and 2.5 m deep was dug. The walls of the trench were reinforced with bulkheads. Steel frames were laterally pressed into the undisturbed soil as side tunnels through three windows (0.7 m high and 1.55 m wide) with a vertical spacing of 1.4 m. The soil inside the frames was simultaneously removed. The steel frames were 1.54 m wide, 0.7 m high and 1.76 m long, and were open at the front and the back.

The Suction Units. The ceilings of the steel frames were pre-perforated in a certain pattern (Figure 1b), through which spherical suction candles (P80, KPM), 5.5 cm long and 20 mm i.d. (Figure 1a) were pressed into pre-drilled boreholes of 1.9 cm i.d., producing an excellent capillary contact. The average catchment area of one suction cup was approx. 0.01 m^2. The average hydraulic conductivity was higher than 30 mL d^{-1} kPa^{-1} yielding an area-related conductivity of 3 mm d^{-1} kPa^{-1}. The whole sampling unit will be called suction base and the three replicates will be denoted as BSB I-III (Birkenheide Suction Base).

The tension which was permanently applied to the suction cups was the average of six pressure-transducer-tensiometers which were built in the undisturbed soil beside and between the suction units at the reference depth of 1.3 m. A control unit regulated the underpressure of a 20 L vacuum reservoir to the target value.

Application and Sampling Areas. The application area for the chemicals was vertically situated above the center of the suction units (Figure 1a) and corresponded to the lysimeter surfaces. To satisfy the safety requirements of the registration authorities, three steel rings 45 cm high and 1 m i.d.were inserted 30 cm into the soil to mark the application areas and to avoid ^{14}C-labeled pesticide run off.

The sampling areas were partitioned into many subsectors (see Figure 1b) whereas the highly resolved areas beneath the application areas were called *central collecting areas*.

Experimental Procedures. The application of the chemicals was carried out on November 22, 1994 to bare soil. First, the plots were treated with bromide by evenly spraying the solution using a 5-L garden hose. The application solution contained 55.7 g bromide per kg of solution. A total mass of 24 g bromide per plot was applied (30 g m^{-2}). The herbicide was applied with a special spraying device which contained a commonly-used hollow-cone nozzle (AMPT 208) and provided for a minimal void volume.

Tillage and cropping was managed corresponding to standard agricultural practice. The lysimeter and field plots were fallowed during the winter seasons. During the vegetation periods summer rape (April - August 1995) and summer wheat (March - September 1996) were cropped. Shallow tillage was carried out before to and after cropping. The plots were hand weeded.

Preliminary irrigation of about 30 mm was carefully carried out to all plots, to obtain similar water contents in the reactive zone. During the experiment, additional irrigation was carried out to guarantee a monthly precipitation equivalent to a minimum total precipitation of 800 mm $year^{-1}$. Differences between the precipitation at the experimental sites were compensated for. The lysimeters were irrigated manually using a watering can which applied single pulses of 1 mm. The irrigation at the field plots was carried out with an ordinary lawn sprinkler, revealing a CV of approx. 20%.

Leachate sampling was carried out weekly during the drainage period between December and May and with larger time intervals in summer, depending on the drainage rates.

The leachate was brought to the laboratory, and after the determination of the drainage volume, every sample was analyzed for ^{14}C-activity and bromide. For extraction and chromatographical analysis the spatially resolved samples were combined.

Accompanying Measurements. The climatic measurements at both locations (lysimeter station and field station) included the air temperature, the rel. humidity, the natural precipitation and the wind velocity. Additionally, the soil temperatures at 10, 30 and 80 cm were recorded.

Soil moisture was measured only at the field station at Plot II using the time domain reflectometry technique (Moisture Point TDR, MP 917) at 5 depths with 25 cm vertical spacing.

The undisturbed Field. A 30 m^2 field plot was situated approx. 7 m away from the field research station with the suction units.

Bromide was applied simultaneously to the lysimeters and suction bases using the same dose and application rate (55.7 g per kg solution and 30 g m^2). The application was carried out with a special cell-spraying device.

Three sampling campaigns were started; three months (2-26-1995), six months (5-23-1995), and ten months (9-26-1995) after the chemical application. The soil samples were randomly taken from the crossing-points of a regular grid with 0.4 m spacing. On the first date, 15 cores were taken, whereas on the second and third date the sample number was reduced to 10 cores.

The sampling was managed using a motor driven rotating auger (Humax) 1.3 m in length and with an inner diameter of 8.6 cm. After sampling, the bore holes were immediately refilled.

The soil cores were sectioned into 10 cm increments and for the first 2 sampling campaigns the increments of the corresponding depths were combined. For the last sampling date, however, the single cores were analyzed seperately. For analysis, the soil was air dried and sieved.

Results

Accompanying Measurements. Due to the additional irrigation the monthly precipitation at both sites was almost identical, resulting in sums of 1,624 mm and 1,630 mm (including irrigation) for the lysimeter and the field station, respectively. However, the rainfall intensities were sometimes different and mostly higher at the lysimeter station.

Comparison of the other climatic parameters revealed that the rel. humidity as well as the the air temperature were almost parallel with yearly mean values of 83% and 82%, and 10.1 °C and 10.4 °C respectively.

In contrast, both the wind velocity and the solar radiation were considerably higher at the field station due to the shading effects of the buildings next to the lysimeter station and the wire mesh cage that encased the lysimeter station. The average wind velocity was 1.4 m s^{-1} at the field station and 0.9 m s^{-1} at the lysimeter station. The solar radiation revealed a mean value of 99 W m^2 at the lysimeter station and 121 W m^2 at the field station. In contrast, the soil temperatures at all depths were almost identical.

The Water Balance. With regard to the water balance, the subject of interest is a defined soil volume 1.3 m in height and with a surface area of 0.8 m^2 (lysimeter) or 2.7 m^2 (suction unites). Since lysimeters are a semi-closed system which is only open at the upper and the lower boundaries (the soil surface and the lysimeter base), the water balance equation can be written as:

$$\Delta S_{lys} = P - ET - D \tag{1}$$

where ΔS_{lys} is the change of water storage within the lysimeter soil core, P is the precipitation, ET the evapotranspiration and D the drainage related to the same time interval may be understood as the average volumetric water content (θ_{mean}) multiplied by the depth of the investigated soil profile. Regarding the lysimeters, all components of the water balance equation were directly measured except the ET which could be calculated from the other quantities. The accumulated ET was almost identical for all lysimeters. As an example, the complete water balance of MRL II is exhibited in Figure 2.

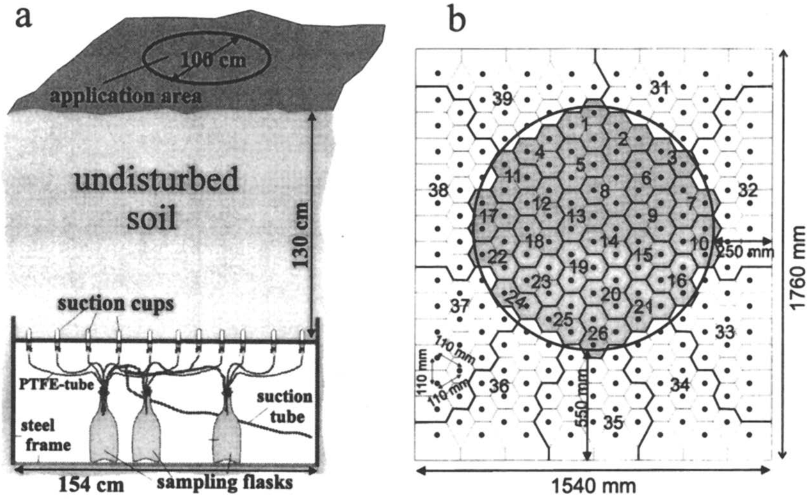
a
100 cm
application area
undisturbed soil
130 cm
suction cups
PTFE-tube
suction tube
steel frame
154 cm
sampling flasks
b
31
39
38
32
37
33
36
34
35
250 mm
110 mm
550 mm
1760 mm
1540 mm

Figure 1. The method of leachate sampling (a). Arrangement of the suction cups and the sampling sectors (b).

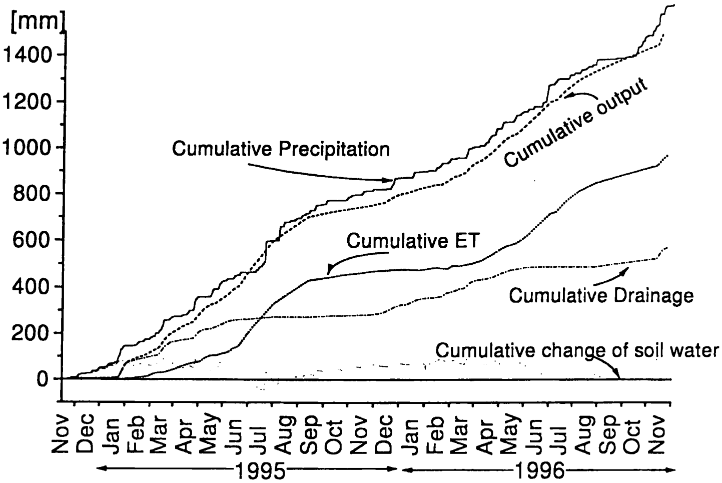

Figure 2. Example of the lysimeter water balance (MRL II).

In contrast to the lysimeters, changes in ΔS of the suction plots, which represent a completely open system, could also result from lateral percolate fluxes into or out of the soil volume under consideration. Thus, one has to add an additional unknown, non-measurable term to the water balance equation yielding $\Delta S_{field} = P - ET - D + F_l$, where F_l is the sum parameter of the lateral in- and outgoing fluxes. The lower boundary of both systems allowed only water outflow, since no possibility for capillary rise existed.

The comparison between the cumulative drainage of both systems (Figure 3) showed that the leachate outflow from the lysimeters was considerably higher than from the suction units (see also Table III). Two replicates of both systems each showed an almost parallel course of the drainage curves whereas MRL I revealed a significantly higher and BSB I a markedly lower leachate outflow. The difference of MRL I to the other lysimeters was caused by an earlier start of drainage outflow, whereas BSB I revealed a permanently lower drainage rate than the other suction plots.

Bromide Leaching

Accumulated Outflow. The cumulative bromide outflow is shown in Figure 4. Following the cumulative drainage, the lysimeters revealed significantly higher bromide recovery after 2 years.

More than two-thirds of the total outflow was collected during the first drainage period. The outflow curves of the lysimeters were almost identical at least for the first year. With respect to the suction plots, BSB II showed a higher bromide outflow of approx. 20% during the whole experiment.

In contrast to all other plots, the bromide outflow of BSB I was restricted to the first experimental year and remained at a fixed level of 37% of the bromide applied.

Bromide Breakthrough Curves (BTC). Figure 5 shows the typical shape of the bromide BTCs for the lysimeters and the suction units. At both systems the Br^- outflow started 70 days after chemical treatment, by which time approx. 180 mm precipitation had been infiltrated.

The peaks of the BTCs always corresponded to high drainage events which were the result of heavy rainstorms. For times of low drainage rates the Br^- concentration in the effluent decreased. In contrast to the lysimeters, the shape of the suction base BTCs were more asymetric and revealed much higher concentrations during the first drainage event.

Nevertheless, the highest bromide concentrations in all plots were in a comparable range between 100 and 200 mg L^{-1}. This was approx. 300 times smaller than the concentration of the application solution.

Leaching of the ^{14}C-Labeled Substances

Accumulated Outflow of the ^{14}C-Labeled Substances. The cumulative outflow curves of ^{14}C-activity and benazolin (Figure 6) demonstrate that there were great differences between the total amount collected and the dynamics of the time-related output.

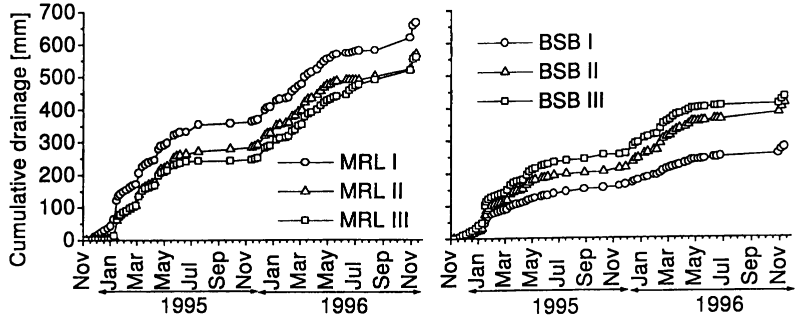

Figure 3. Cumulative output of leachate during the two experimental years.

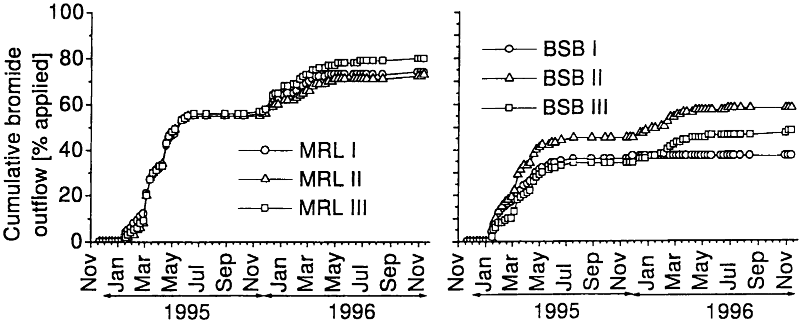

Figure 4. Cumulative bromide outflow during the two experimental years relative to the mass applied.

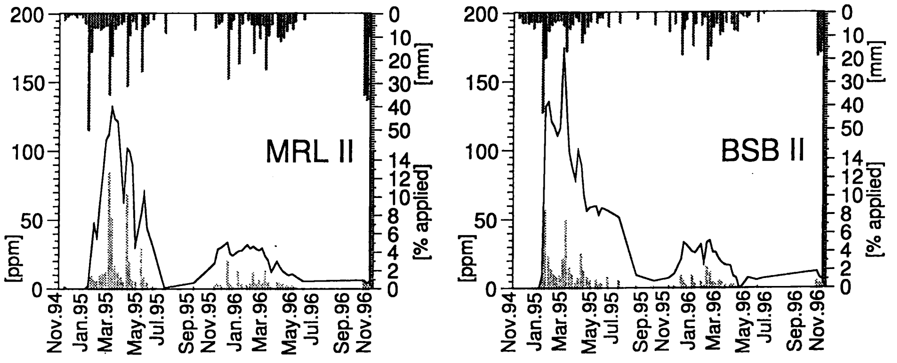

Figure 5. Typical BTCs of bromide against time. The light gray columns indicate the mass of bromide collected at each sampling date. The dark gray columns represent the leachate collected at each sampling date.

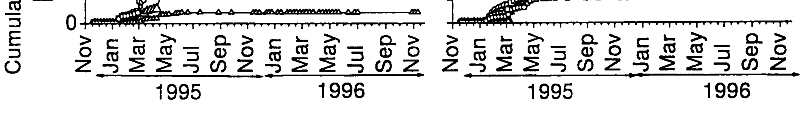

Figure 6. Cumulative outflow of the ^{14}C-activity and benazolin. The large symbols mark the ^{14}C-activity and the tiny symbols mark benazolin, respectively.

At the beginning of the drainage period benazolin was the dominant fraction for all plots. However, for MRL I and MRL II, the cumulative outflow of the non-identified fraction exceeded the amount of ^{14}C-benazolin, whereas for all other plots benazolin remained the highest fraction of the total sampled ^{14}C-activity (see also Table III). At all plots more than 85% of the total sampled benazolin was collected during the first six months following application.

Despite the pronounced differences between the single replicates, no substantial differences between the lysimeter and the suction base system can be noticed with respect to the cumulative outflow of the ^{14}C-labeled compounds. The plots which reveal the most similar output curves were MRL III and BSB II. They did not only result in comparable total outputs of ^{14}C-activity and benazolin, but they also showed similar dynamics of the cumulative outflow. It must be mentioned that for all plots, the breakthrough of the ^{14}C-labeled substances began at the same time as the bromide outflow during the first important drainage event (69 days after chemical application), revealing that parts of the reactive chemicals were transported without any retardation.

The outflow data of the two systems are summarized in Table III. The cumulative drainage and bromide outflow showed large differences between the mean values but relatively small standard deviations. In contrast, the variation between the replicates were enormous with respect to the ^{14}C-activity and benazolin, whereas the mean values of the system were almost identical.

Table III: Statistics of the lysimeter and suction unit outflows. Values in parenthesis are % of the amount applied.

	Mean		CV		*t*-test
	MRL	BSB	MRL	BSB	
Drainage [mm]	597.3	372.1	9.7	22.7	x
	(36.8)	(22.9)			
Bromide [mg m^2]	23.3	14.6	4.9	19.7	x
	(77.1)	(48.9)			
Br^- Conc. [mg L^{-1}]	39.3	39.8	11.9	10.8	
^{14}C-activity [kBq m^{-2}]	4932	4562	42.4	53.2	
	(5.40)	(4.85)			
Benazolin [µg m^2]	1081	1347	90.3	62.0	
	(2.41)	(2.94)			

x: Differences at 5% level xx: Differences at 1% level

Finally, Table IV shows the correlations between the total outflow of leachate and chemicals concerning the six different plots of the two systems. A close correlation exists between drainage and bromide as well as between ^{14}C-activity and benazolin outflow. However, the cumulative ^{14}C-activity, as well as the benazolin in the effluent, was correlated neither to the drainage nor to the bromide outflow.

Table IV: Correlation matrix of the total outflow related to the 6 plots of both systems.

	Drain.	Bromide	^{14}C-activity	Benazolin
Drainage	1			
Bromide	0.92**	1		
^{14}C-activity	0.10	0.34	1	
Benazolin	-0.24	0.03	0.93**	1

* P<0.05 ** P<0.01

Spatial Variability of Soil Water and Solute Movement in the Grid Suction Bases

Cumulative Outflow Patterns. Since the drainage volume, the bromide and ^{14}C-radioactivity concentration were determined for each sampling sector of the suction units (Figure 1b), it was possible to reflect the spatially resolved leachate and solute fluxes at the given cross-section. As an example, the cumulative drainage and solute flux patterns of BSB II are given in Figure 7.

Large spatial heterogeneity of the leachate fluxes existed at the sampling depth. Areas of very low drainage flux rates alternated with spots where most of the collected leachate passed through the cross-section. Differences between the areas of low drainage flux rates and the spots of highest drainage rates were at least of one order of magnitude.

The output of the chemicals which were applied to a 0.8 m^2 surface occurred in high concentration at specific outflow centers. Only negligible amounts of solutes were collected outside the central collecting area. Therefore, lateral redistribution of the solutes caused a funnel-like concentration instead of lateral dispersion. The concentration of the spatial solute output to 'hot spots' was more pronounced for the outflow of the ^{14}C-labeled compounds than for bromide. More than 50% of the total ^{14}C-activity collected was sampled from less than 20% of the application area (which corresponded to the central collecting area) and from 50% of the sampling area more than 90% was sampled.

The Field Experiment. Bromide depth distributions from the field were obtained at three dates to compare the (i) mass of bromide recovered within the first 1.3 m of the field, with the mass which was found in the effluent of the lysimeters and the suction plots (Br^- that was tranlocated deeper than 1.3 m). The concentration profiles are plotted in Figure 8 and their characteristics are given in Table V.

The balances for the sampling dates become poorer with time and the depth of translocation. Between 114 mm and 152 mm (cumulative drainage and cumulative precipitation, respectively) net infiltrated water was responsible for the bromide distribution of the first sampling date. If one assumes that the pore water velocity (V) is given by the depth of the bromide pulse (center of mass) per time, one may calculate the transport volume as the quotient of the net infiltration flux (j_w) and the pore water velocity (V). The values range from 0.17 to 0.23 which is in a comparable range than the values of the volumetric water content measured with the TDR (not

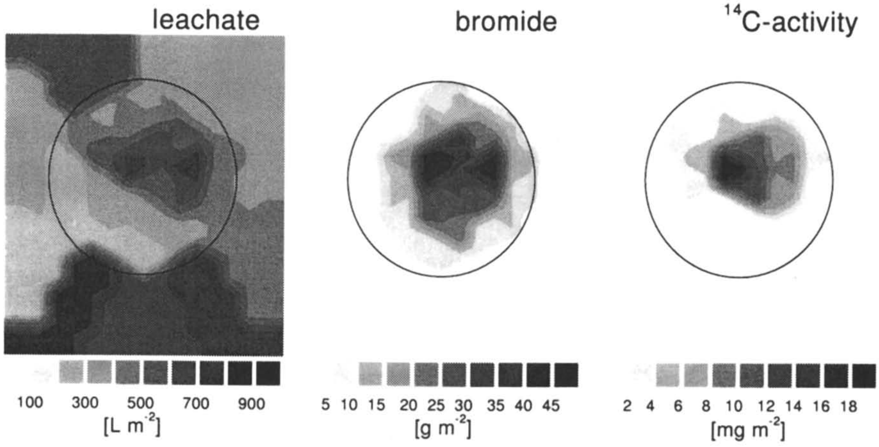

Figure 7. Patterns of the cumulative spatially resolved leachate (a), bromide (b) and ^{14}C-activity output (c) in a.i.-equivalents of BSB I after 2 years.

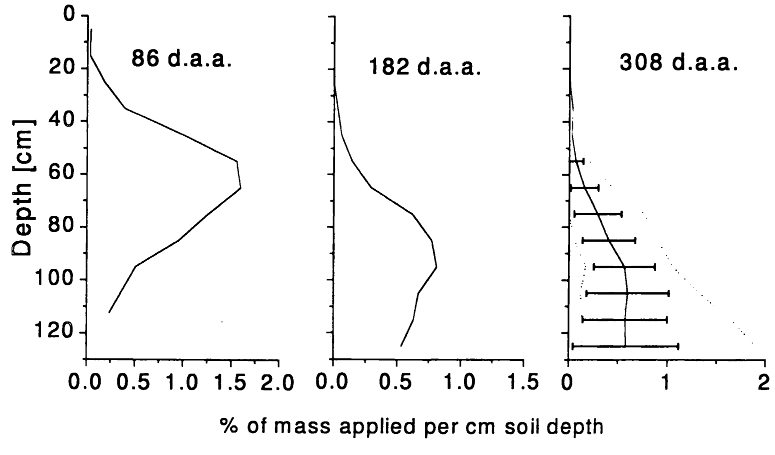

Figure 8. Bromide concentration profiles of the field down to 130 cm. The horizontal lines represent the standard deviation and the dotted lines connect the lowest and the highest concentrations at each depth.

described in this paper). This indicates that most of the soil water of the upper layers contributed to the bromide movement.

Table V: Statistics and properties of the bromide profiles collecteded at three dates from Field I and II. Recovered bromide amounts are expressed as % of the mass applied.

Days after application		86	182	308
n		15	10	10 (10 x 1)
Average recovered mass	[%]	81.0	45.6	33.3 (18.1)[†]
Range of recovered mass	[%]			11.1 - 75
Mean - vertical[‡]	[cm]	>67.1	>> 94.0	>> 98.7
Cumulative Br$^-$ outflow of the suction units	[%]	10.8	34.1	37.8
Field - Suction unit - Balance	[%]	91.8	79.7	71.1

[†] standard deviation of the masses from the the different cores.

[‡] the values are exclusively related to the distribution within the upper 1,3 m.

Discussion

Bromide Transport in the Field and the Suction Plots. A leaching experiment with bromide was simultaneously carried out at the undisturbed field and the suction plots to test the validity of the suction bases. The bromide balances were excellent for the first sampling but became poorer for subsequent samplings.

It can be assumed that this is not caused by different transport processes, but rather by an incomplete description of the actual bromide distribution within the undisturbed field due to the limited number of soil samples. This hypothesis is confirmed by (i) the large variation of the masses recovered in the different cores of the last sampling campaign (CV > 50%) and (ii) the findings from the solute outflow patterns. Since it was shown that the solute transport at least through the lower soil layers was restricted to small regions, the likelihood of obtaining a representative image of the ensemble, with a given number of samples decreased drastically.

To summarize, no substantial differences were observed between the leaching process in the undisturbed field and the suction plots. Thus it can be assummed that the suction bases were able to represent the undisturbed field.

Nevertheless, the comparison of the bromide depth profiles with the bromide BTCs of the suction units exhibited additional information about the transport processes. While the center of the bromide pulse in the field was still above the 1.3 m sampling depth after 10 months, the highest concentration of the BTCs (which normally represents the breakthrough of the center of the pulse) was already reached after 4-5 months.

To explain this behavior, one has to consider that from the suction units a drainage flux weighted solute concentration (flux concentration) was obtained. In contrast, the analysis of soil cores always gives the resident concentration, which is the solute mass per soil or soil water volume (*7*). The distinction between the different types of concentrations becomes important if (i) the dispersion of the transport process is large (*8*) or if (ii) the flow field is heterogeneous (*9*). The large spreading of the bromide pulse as well as the drainage patterns of the suction bases indicate the occurrence of both effects.

Since the soil of the lower layer was more structured, bypass flow could occur. Hence, highly concentrated percolate from the layer interface was quickly translocated to the sampling device, whereas the center of the pulse could remain within the investigated profile.

These observations demonstrate an additional benefit of the lysimeter technique estimating the chemical concentration of the soil solution which reaches a certain depth (flux concentration). In the present study this would not have been possible by the analysis of soil samples from the field (resident concentration).

Solute Fluxes of the Lysimeters and the Suction Plots. Significant differences were found between the accumulated drainage and the bromide outflow of the two systems. Since in both devices, capillary rise through the sampling cross-section was not possible, the differences could only be caused by higher evapotranspiration or lateral soil water and solute outflow; but the solute outflow patterns show that lateral fluxes out of the system were unlikely. However, the higher wind velocity and the higher average solar radiation at the field station imply higher transpiration rates. This may serve as the most important explanation for the different drainage amounts.

Besides, the infiltration rates during heavy rainstorms were mostly higher at the lysimeter station. These events caused immediate leachate outflow by displacement and bypass flow, and may have contributed to the higher drainage outflow of the lysimeters.

In contrast to the bromide leaching, the ^{14}C-radioactivity and the benazolin outflow were almost identical for both systems. The high variation between the replicates as well as the lack of correlation to the bromide or leachate outflow demonstrates that bio-chemical processes on a larger scale must have crucially influenced benazolin leaching. If the differences had been caused by physical variabilities of the flow regime they would also have influenced the bromide transport. Similar findings were obtained by Bergström and Jarvis (*10*). They found pronounced differences between the leaching losses of dichlorprop and bentazon for replicated lysimeters whereas the outflow of a conservative tracer (^{36}Cl) occurred similarly.

Nevertheless, the simultaneous arrival of parts of the conservative tracer and benazolin at the sampling depth which was found with most of the plots, demonstrated that parts of the herbicide passed the soil without any interaction with the soil matrix.

That non-chromatographical transport of a sorbing chemical can only be explained by non-equilibrium sorption kinetics, i.e., at high flow rates benazolin had insufficient contact time with the sorption sites. Therefore, the sorption equilibrium could not be achieved by either chemical (reaction time) or physical means (diffusion - mass transfer limited processes) (*11*).

Spatial Variability. Lateral redistribution of water and solutes was always reported from leaching studies where grid lysimeters were used (*12-15*). In all studies, a high proportion of the leachate and solutes were sampled in a small proportion of the sampling area, regardless of the soil type, texture and structure and the pre-treatment of the soil (e.g. tillage, wetting).

The influence of the infiltration rate on the drainage and solute outflow patterns was reported previously (*16*). Therefore, rainfall events of different intensities cause the solutes to be transported within different pathways with different hydraulic and bio-chemical properties. Thus, it must be assumed that independent from the total infiltration (annual rainfall) the leaching amount of chemicals may vary widely, depending on the rainfall intensity and the temporal distribution of annual precipitation. Consequently, the kinetic effects of sorption become more increase with higher pore water velocity.

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Chapter 11

FELS: A Comprehensive Approach To Studying the Fate of Pesticides in Soil at the Laboratory, Lysimeter and Field Scales

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Lysimeters containing a soil monolith are generally recognized and used to study the environmental behaviour of pesticides in accordance with good agricultural practice. In order to validate the transfer of lysimeter data to the field/region scale, an extensive experiment was set up consisting of a 1-ha experimental field plot with five sampling tubes, a small plot experiment, 12 lysimeters, a measurement trench with 102 time domain reflectometry sensors (TDR) and 21 temperature sensors and a weather station. The leachate in the field and small-plot experiment is obtained using tensiometer-controlled ceramic plates. In addition to a mobile and an immobile test substance for determining mass transport, several water tracers are used over the three-year test period. A preliminary experiment for the further characterization of the test site and test systems was started in March 1997 with the application of 2,6-difluorobenzoic acid. Complementary laboratory studies are performed for process identification and generation of input parameters for simulation models.

For active ingredients showing some leaching potential practice-like lysimeter experiments using radiotracer techniques play a central role. Lysimeter experiments using ^{14}C-labelled pesticides yield comprehensive information on the uptake of the respective compounds by treated and untreated rotational crops, the residue behaviour of pesticides in soil and leaching (1). With the addition of a wind tunnel erected over a lysimeter, a complete mass balance including volatilization and mineralization can be achieved (2). In 1990 the German government authorities published a guideline for lysimeter studies (3) required for those compounds which show a potential for leaching. As far as the dissipation in soil and residue level in treated plants are

In The Lysimeter Concept; Führ, F., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 1998.

concerned, data with the herbicides metamitron and methabenzthiazuron demonstrated good agreement between lysimeter and field studies (4, 5). As far as leaching is concerned, the situation is more complicated due to the different processes involved. In order to achieve a better understanding of the relevant processes concerning the persistence and especially the translocation of pesticides on different scales, the FELS study (Field - LysimEter - Laboratory - Simulation) was conceived as a combination of laboratory, lysimeter and field studies, which may provide the basis for a more complete elucidation of the situation. Up to the present, it has not been clarified whether and under what conditions the lysimeter constitutes a representative field compartment with respect to the leaching behaviour of a pesticide especially in heavy soils. Possible differences between the lysimeter and the field are attributable to the variability of the soil, the different dimensions of the test systems and unrealistic lower boundary conditions of the lysimeter. The major goals of the FELS study are as follows:

Scaling from Lysimeter Scale to Real Field Situation. The interpretation and verification of the TRANSFERABILITY of results from lysimeter experiments based on the comparison of water movement, solute transport and degradation processes at the lysimeter and the field scale. On the basis of the experimental data obtained, a simulation-model-based comparison of lysimeter and field is to be carried out.

Process Characterization and Process Description. Another important aim is to identify characteristic processes influencing the behaviour of pesticides in the agroecosystem and in the lysimeter. In essence, this implies a determination of the variability in space and time of relevant, already known processes in the atmosphere-biosphere-pedosphere system and a description of their interactions and synergetic effects. In this connection, the quantification of the influence of different state variables on water transport and the residue and transport behaviour of pesticides in the field and lysimeter play a particular role. It is therefore necessary to determine the spatial variability of soil temperature and soil humidity. Another basic requirement is to determine the space-time variability of important soil properties (soil density, C_{org} content, hydraulic conductivity, etc.) and to describe it using geostatistical methods.

Simulation. The data sets derived will be used to verify and further develop existing simulation models describing the behaviour of pesticides in the agroecosystem. The validity is assessed and the sensitivity of simulation models predicting the leaching behaviour of pesticides is determined taking into account the natural variability of extrinsic and intrinsic factors of influence (soil properties, climatic factors, physico-chemical properties of the active ingredient, cultivation procedures).

Experimental Design

For the purposes of the FELS study, an extensive study (Figure 3) was set up on a 7.5-ha plot in Merzenhausen, approx. 10 km northwest of Forschungszentrum Jülich GmbH, Jülich, Germany (coordinates: 6 54′ 35″ E and 50 54′ 41″):

- trench with 102 TDR and 21 Pt-100 sensors,
- a 1-ha field plot with five sampling tubes, field plot with different pretreatment (bare over one year versus continuously cropped)
- a small-plot experiment with three replicates next to the field plot and
- 6 lysimeters at the field site, as well as
- 6 lysimeters in the open-air control area of the ICG-5 at the Research Centre.

The soil type of the arable site is to be described as an orthic luvisol from eluviated loess according to FAO classification. This soil type (clayey silt) is one of the most fertile arable soils and is widely found in the Federal Republic of Germany (6). The setup and experimental procedure is oriented to the criteria enabling a geostatistical evaluation and use of the results in simulation models.

Characterization of the Field Plot. In order to exactly characterize and identify any major disturbances and differences, a grid of 10 x 10 m was surveyed on the 1-ha experimental field plot. In June 1994, soil samples were taken down to a 60-cm depth on the grid points and divided into segments of 30-cm length. The C_{org} content (Figure 1 and 2), the cation exchange capacity (CEC) and the pH value were determined for each individual segment. At the same time, soil-physical parameters (hydraulic conductivity, pF characteristic, penetration resistance) were measured. The soil-chemical and soil-physical parameters characterize the soil of the field plot as relatively homogeneous and exhibiting no major areas with deviating properties.

In order to describe possible preferential flow paths for the translocation of soil solution in the soil, Brilliant Blue FCF colorant was applied in July 1995 on two

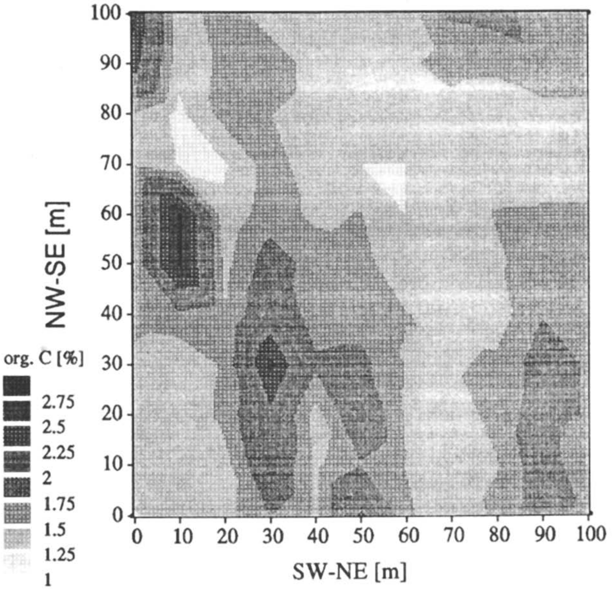

Figure 1. Variation of Organic Carbon in the Field Plot in the 0-30-cm Soil Layer.

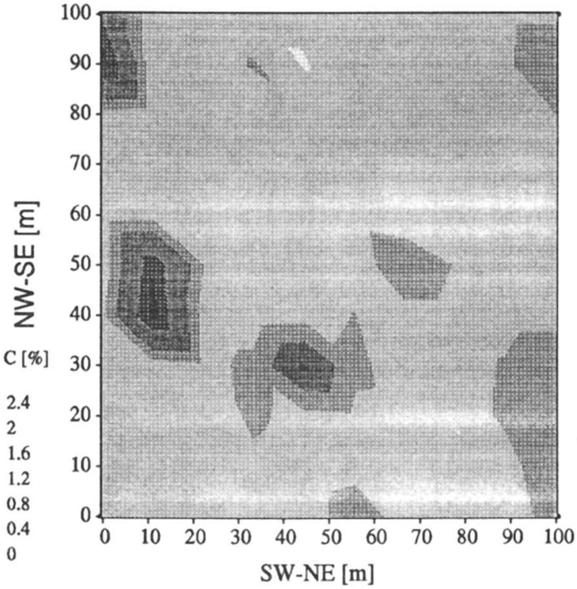

Figure 2. Variation of Organic Carbon in the Field Plot in the 30-60-cm Soil Layer.

subplots (1.5 m x 1.5 m each) by a 30-mm irrigation in two hours. With respect to the infiltration of Brilliant Blue, pronounced fingering was observed. The maximum infiltration depth was 30 cm for this experiment after 1 day after application, whereas the average infiltration depth was 5 cm.

Description of the Experimental Equipment. The field experiment, the small plot experiment and the lysimeter experiment are arranged next to each other (Figure 3).

Field Experiment. Five tubes were installed for sampling the leachate in the field experiment (Figure 3 and 4). For this purpose, five steel cylinders of 1.6-m diameter and 2.0-m height were vibrated 2.5-m deep into the soil and stepwise excavated during installation. The tubes were covered with a steel plate, onto which a 0.5-m high entrance hatch was welded. In order to avoid backwater and lateral runoff along the side walls of the sampling tubes, the steel covers were provided with several holes to drain the water. A cylindrical metal sheet (50-cm height, ca. 1.5 m diameter) was set on top of the steel cover and sealed at the bottom. Then the soil was backfilled.

Six windows (0.3 m x 0.4 m) were cut into the steel wall of the pits at two levels ('gallery'), namely at 0.40 m and 1.20 m depth. For leachate sampling 0.70-m long tunnels were cut through the windows with the aid of supporting frames, and ceramic plates with a diameter of 27.0 cm were clamped against the top at the tunnel end. The total number of individual ceramic plates installed is 60 (5 tubes with 6 plates at each of the two depths). The ten-minute mean value of three pressure gauge tensio-

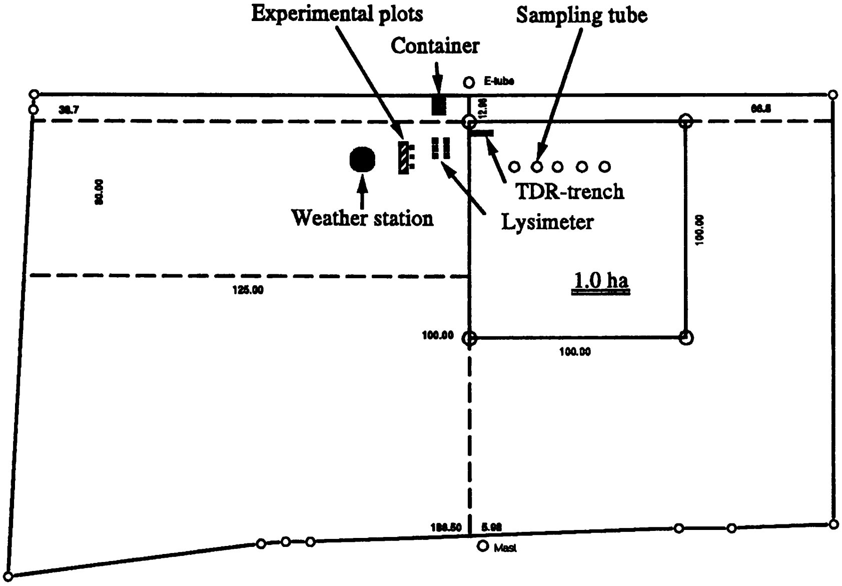
Experimental plots
Container
Sampling tube
E-tube
38.7
12.96
66.8
90.00
Weather station
TDR-trench
Lysimeter
100.00
1.0 ha
125.00
100.00
100.00
188.50
5.98
Mast

Figure 3. Layout Plan of the Experimental Field Plot, the Small Plots and the Lysimeters as Well as the Other Installations at the Merzenhausen Site (dimensions in m).

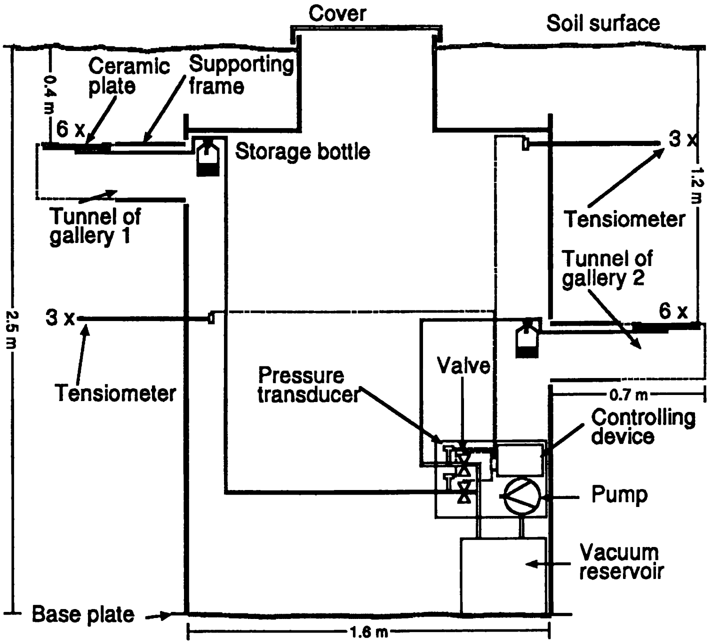
Cover
Soil surface
Ceramic plate
Supporting frame
0.4 m
6 x
Storage bottle
3 x
1.2 m
Tunnel of gallery 1
Tensiometer
Tunnel of gallery 2
2.5 m
3 x
6 x
Tensiometer
Valve
Pressure transducer
0.7 m
Controlling device
Pump
Vacuum reservoir
Base plate
1.6 m

Figure 4. Cross-Section of a Sampling Tube.

meters per 'gallery' level determines the target value for suction control of the ceramic plates (Figure 4), whereas the water is collected continuously. Each tube is equipped with a suction control unit to record the tensiometer data and to control the respective tension for the two suction plate galleries.

In contrast to the lysimeters and small plots, periodical soil sampling is carried out in the field experiment to measure the degradation and translocation of the applied active ingredients as well as the movement of the water tracers applied.

Small-Plot Experiment. The small-plot experiment constitutes the link between field and lysimeter experiments. This experimental design includes the advantages as well as the limitations of field and lysimeter, with the exception of the lower boundary conditions (Table 1). For the small-plot experiment (Figure 5) an installation and maintenance ditch of 10 m x 3 m x 2.5 m (l x w x d) was established. From there three steel frames with a size of 1.2 m x 2.44 m x 1.0 m (w x l x h) were horizontally driven into the undisturbed soil and simultaneously excavated. In the front part (1.24 m) of the frame's ceiling 16 chessboard-like recesses provide access to the undisturbed soil at a depth of 1.1 m where 16 square ceramic plates (25 cm x 25 cm) were installed to collect soil solution. The total sampling area thus comprises approximately 1.49 m^2. The suction continuously applied to the ceramic plates is controlled in analogy to the sampling tubes. At the soil surface a total of three square, 50 cm high stainless steel frames with a surface area of 0.5 m^2 were exactly centred above each 1.49-m^2 sampling area and pressed approximately 30 cm deep into the soil. They delimit the application area and ensure that the ^{14}C-labelled active ingredient is not washed off due to runoff.

During the experiment, no soil samples will be taken from the small plots to prevent any disturbance of the water and mass transport.

Table 1. Advantages and Limitations of Field and Lysimeter Experiments.

Lysimeter	Field
Advantages	Advantages
use of high amounts of radioactivity	real field situation
agricultural practice	real farming practices
mass balance	
repetitions	

Limitations	Limitations
unrealistic lower boundary conditions (disturbed drainage)	no mass balance
restricted dimension (compression, cracks, wall effects as a result of filling procedure)	no or limited use of radioactivity no information on bound residues detection limit in soil

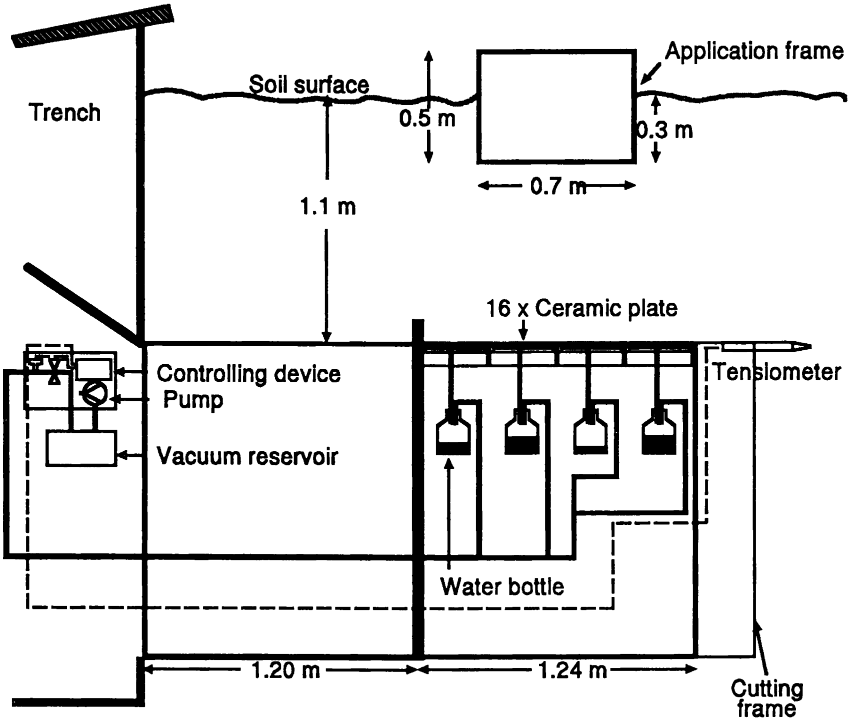

Figure 5. Cross-Section of the Small-Plot Experiment.

Lysimeter Experiment. In the FELS study, square lysimeters made of stainless steel are being used, which contain 1.10-m-deep soil monoliths (1, 7). The experiment was started with ten 1-m^2 lysimeters and two 0.5-m^2 lysimeters as described by Führ et al. in this volume. These lysimeters were filled in autumn 1993 at the Merzenhausen field site in the immediate vicinity of the experimental field plot. Until October 1995 the lysimeters were controlled with respect to cracks, compression and abnormal amounts of leachate in the lysimeter station of the ICG-5 at the Research Centre. All arable measures were carried out in conformity with the field site. With respect to the leachate volume, none of the 12 lysimeters showed anomalies which would have justified an exclusion from the experiment (Figure 8). In October 1995 the lysimeters were grouped by six joining those with comparable leachate volumes. One set was installed in the immediate neighbourhood of the 1.0-ha field plot and the small-plot experiment. The other set of six lysimeters remained in the Research Centre where they were treated in parallel to the lysimeters in the field.

In the course of the experiment, periodical soil sampling will be carried out in two lysimeters. In the other ten lysimeters only the leachate is collected and analysed. Sampling of the soil layers of all soil monoliths will be carried out at the end of the experiment.

Laboratory. As a complement to the field, small-plot and lysimeter experiments, characteristic processes are being studied in detail on a laboratory scale concerning the fate of the two test substances in the agroecosystem. Different state variables (humidity, temperature) and different variants are being characterized in more detail with respect to active ingredient application (mixed-in, surface-applied) in several small-column and degradation experiments. In soil column experiments (length: 40 cm, diameter: 20 cm, volume: 12.6 L, (8)) transport parameters for the simulation models and sorption parameters for the test substances are determined using water tracers.

Test substances and water tracers. In order to check and optimize the sampling systems, two test substances are used in the field, in the lysimeters and in the small plots, which should cover the whole spectrum from immobile to mobile translocation behaviour. For this purpose, two urea derivatives were chosen: the non-selective herbicide ethidimuron (ETD) $^{13}C/^{14}C$-labelled in the thiadiazol-2 position, as well as the selective herbicide active ingredient methabenzthiazuron (MBT) (Figure 6). The active ingredient MBT was not radioactively labelled for the experiments. Mobile behaviour is to be expected for ETD on the basis of the product information available. The MBT test substance was classified as immobile due to laboratory, field and lysimeter experiments conducted over many years (4, 5, 9, 10, 11, 12, 13, 14, 15). The two test substances are of similar persistence in soil with their DT_{50} ranging from 60 to 220 days for both compounds.

Different water tracers will be applied at three different times to characterize the water movement and test the different experimental systems. For a system test, 2,6-difluorobenzoic acid was applied in March 1997. In parallel to the application of the two test substances ETD and MBT, the conservative water tracer bromide (KBr^-) will be applied. It is planned to apply chloride and/or D_2O as further water tracers at a later stage of the experiment in order to characterize the water flow patterns at different times..

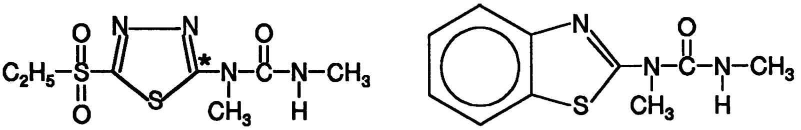

Figure 6. Test Substances Used and ^{14}C-labelling Position (*) of Ethidimuron.

Application. As a preliminary test the application of 2,6-difluorobenzoic acid (DFB) was performed on 3 March 1997 at an application rate of 6.2 g m^{-2} dissolved in 3.15 L m^{-2} H_2O. The application solution was applied with a conventional field sprayer (Douven, 21.0-m folding boom). The aim of this experiment was to test the ceramic plate sampling systems in the sampling tubes of the field experiment and in the small plots and to obtain first information about their water balance, including the lysimeters. The main experiment will be started in November 1997. In the small plots and lysimeters a tank mix of formulated $^{13}C/^{14}C$-labelled ETD and non-labelled MBT will be applied, whereas a non-labelled mixture of the two formulated active ingredients will be sprayed in the field experiment. The application rate of the two test substances will be oriented along the lines of the field application rate of 1.5 kg ha^{-1} ETD and 2 kg ha^{-1} MBT dissolved in ca. 2000 L H_2O. Spray application on the experimental field plot will be performed with the field sprayer already used in the preliminary experiment. An essential part of the concept of the study is the simultaneous application of the test compounds and the bromide onto all test systems. Due to the use of the non-selective herbicide ETD there will be no vegetation at least during the first year after application. As a side effect plant roots will not interfere with the sampling systems, especially relevant for the ceramic plates at 40 cm depth.

Determination of Weather and Soil Parameters. Comprehensive data sets of various weather and soil parameters are needed to describe, evaluate and model processes concerning the transport, sorption/fixation and degradation of pesticides. For this purpose at the filed site as well as at the Research Centre a weather station was set up consisting of a data acquisition system, a pyranometer, several anemometers, a hygrometer, an air temperature sensor and an ombrometer. In addition, a heat flux plate was installed in the field. In order to continuously monitor and record soil temperature and soil moisture distribution and variability over space and time, a ten-meter- long and 1.8-m-deep trench was dug, and a total of 102 TDR sensors (depths: 0.20 m, 0.45 m, 0.60 m, 0.80 m, 1.00 m, 1.50 m) and 21 Pt-100 sensors (depths: 0.05 m, 0.20 m, 0.45 m, 0.60 m, 0.80 m, 1.00, 1.50 m) were installed laterally into the wall, i.e. undisturbed soil. In parallel, 10 TDR sensors and 10 PT-100 sensors were horizontally installed at the same depths in one of the lysimeters at both sites. Additionally these two lysimeters are weighable to determine soil evaporation.

Preliminary Experiments with 2,6-Difluorobenzoic Acid. On 3 March 1997 2,6-difluorobenzoic acid was applied on a 600-m^2 section of the experimental field plot including the five sampling tubes, on the small plots and the lysimeters at an application rate of 6.2 g m^{-2}, dissolved in 3.15 L m^{-2}, corresponding to 62 kg ha^{-1} in 31500 L ha^{-1} water. In the first three-month observation period, 197 mm of precipitation was registered in the Research Centre and 175 mm at the Merzenhausen field site. Precipitation measured at the Research Centre was above the 25-year average, whereas precipitation at the field site equaled the corresponding long term average (Figure 7).

Between 24.6 and 25.7 mm of leachate per small plot was released over the ceramic suction plates of the three small plots during the observation period, a variation coefficient of up to 73% being observed between the individual plates. In parallel, between 10.0 and 14.3-mm leachate was collected from the upper galleries of the sampling tubes and between 10.5 and 20.0 mm from the lower galleries. The variation coefficient between the individual plates was in the range of 90% for the upper and lower galleries.

In the lysimeters, 83 mm of leachate was collected during the same three-months period. The six lysimeters in Jülich furnished a 25% higher leachate volume probably due to the slightly higher precipitation in comparison to the six lysimeters positioned at the field site (Figure 8).

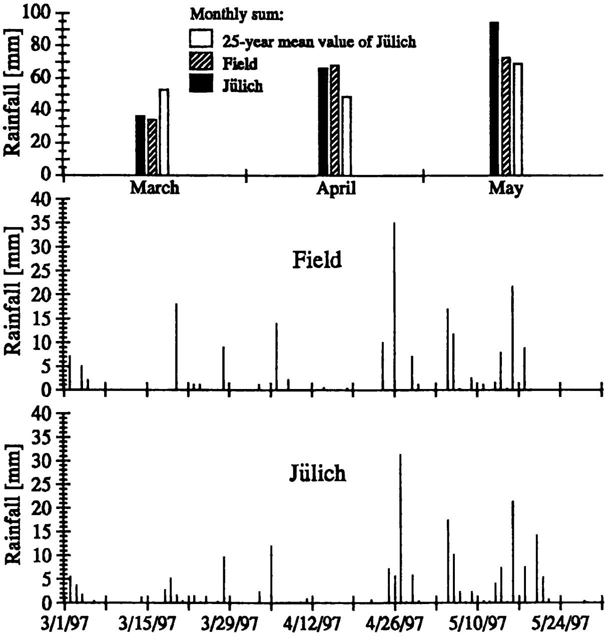

Figure 7. Precipitation Events at the Field Site and at the Research Centre Jülich.

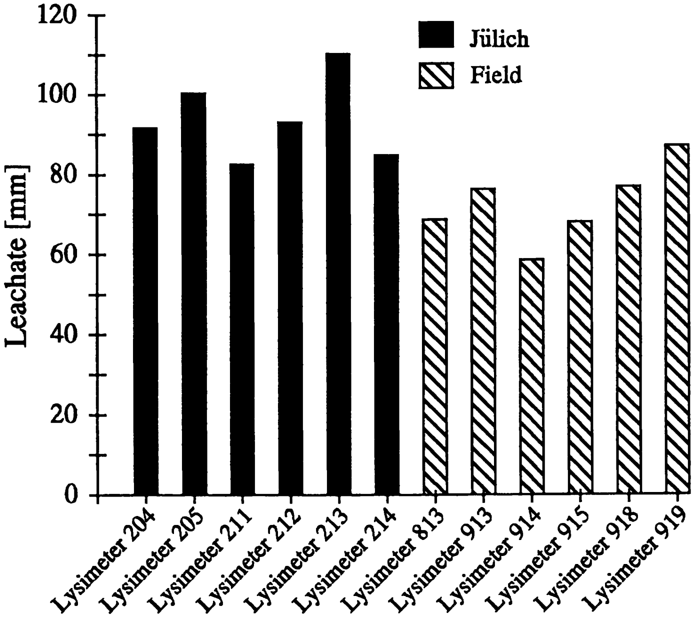

Figure 8. Leachate Volumes of the Lysimeters Installed in the Field and in the Research Centre Jülich.

Conclusions. Based on the results of the preliminary test the sampling systems of the small plot experiment and sampling tubes proved efficient and suitable for practical application. However, it remains to be clarified in the further course of this preliminary experiment how the vacuum control of the ceramic plates of the sampling tubes has to be optimized to ensure representative sampling of soil water.

We are looking forward to elucidating in more detail the flow situation in a structural soil of loess origin on different scales.

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Chapter 12

Measuring Environmental Impacts of Land Use Changes on Water Quality with Lysimeters

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To study and predict environmental impacts of land use changes we operate 200 lysimeters at 6 lysimeter stations. Different types of lysimeters are used to evaluate the effects of intensive and extensive agricultural systems, fallow systems and forestry types on drainage water quality. Lysimeter experiments allow the rapid detection and prediction of the impacts of changes in agricultural management. In particular, they are suitable for studying the transformation and translocation of nutrients and other chemical substances passing through soils and sediments into water systems. The objective of this paper is to discuss a) our different lysimeter set-ups and related experiments, b) the initial results of our lysimeter studies and their impact on land use management and c) the scaling-up of lysimeter data to catchment areas. However, from the point of view of protecting drinking water quality, rotation fallow for one year is not recommended because of the resulting intensified leaching of nitrates.

Agriculture in the former East Germany experienced fundamental changes with German unification in 1990. Policies of the European Community (EC) had to be implemented in the five new German states aimed at reducing agricultural overproduction by various means such as extensive cultivation or taking land out of production for several years. As a consequence, 10 % of the 6.2 million hectares of land previously intensively farmed were abruptly left idle. The question was raised, whether or not nutrients and agrochemicals accumulated in the soil during the former intensive cultivation represent a potential risk for the quality of both surface and ground waters.

In Germany agriculture is directly responsible for more than 50 % of the nitrogen leached into streams and rivers *(1)*. This pollution takes places primarily through a diffuse soil - ground and surface water - pathway *(2)*. Ground water supplies more than 70 % of the drinking water in Germany. Therefore, it is of vital importance to know the quantity and quality of water which leaves the root zone to enter the aquifer and finally the surface water system. Process-oriented lysimeter studies in combination with flow models and verifying field experiments can substantially contribute to knowledge about diffuse pollution and water recharge which is necessary to develop sustainable land management system. Our immediate goal is to establish methods that will allow us to extrapolate lysimeter results to small catchments with similar meteorological and pedological settings.

Description of the Lysimeter Stations and the Experimental Catchment Areas

The UFZ Center for Environmental Research operates 6 lysimeter stations at 3 sites in typical regions of the river Elbe catchment, which is the most important one in East Germany (Figure 1).

The Continuously Recording Lysimeters at the UFZ Lysimeter Research Station in Falkenberg. The 2 lysimeter stations in Falkenberg represent the Elbe catchment in the northern regions of the federal states of Saxony-Anhalt and Brandenburg.

The Station of Large Non-weighable Lysimeters. One hundred and twenty non-weighable lysimeters each with a surface area of 1 m^2, a total depth of 1.25 m and free drainage were constructed in 1983. The lysimeters were filled with disturbed soil profiles (sandy loam, sand, loam, loess) commonly found in the catchment area of the Elbe river and the northern part of East Germany. Between 1985 and 1990 a complex experiment was implemented to develop systems that optimize water management and agricultural production in protected water catchments by minimizing the translocation of relevant macronutrients (N, P, K) from the root zone at high crop yields *(3)*. The soils in the lysimeters were intensively fertilized and irrigated during summer according to common cultivation practices in the former GDR (East Germany). After the reunification of Germany the experiments were adapted to investigate the impacts of changes in agricultural land management (mainly extensification and leaving land fallow) on the water and solute balance.

In 1995 four additional non-weighable lysimeters with a surface area of 1.0 m^2 and a total depth of 1.75 m with free drainage and a system for regulating the water table were constructed. These lysimeters were filled with representative soils and sediments from open-pit brown coal mining near Leipzig. The objective is to measure the ground water recharge in these mining landscapes and to determine the influence of rising ground water tables on the water and solute balance.

The drainage water from each lysimeter is collected in a separate storage container. At least once a month, the volume of water leached is measured and samples analyzed chemically.

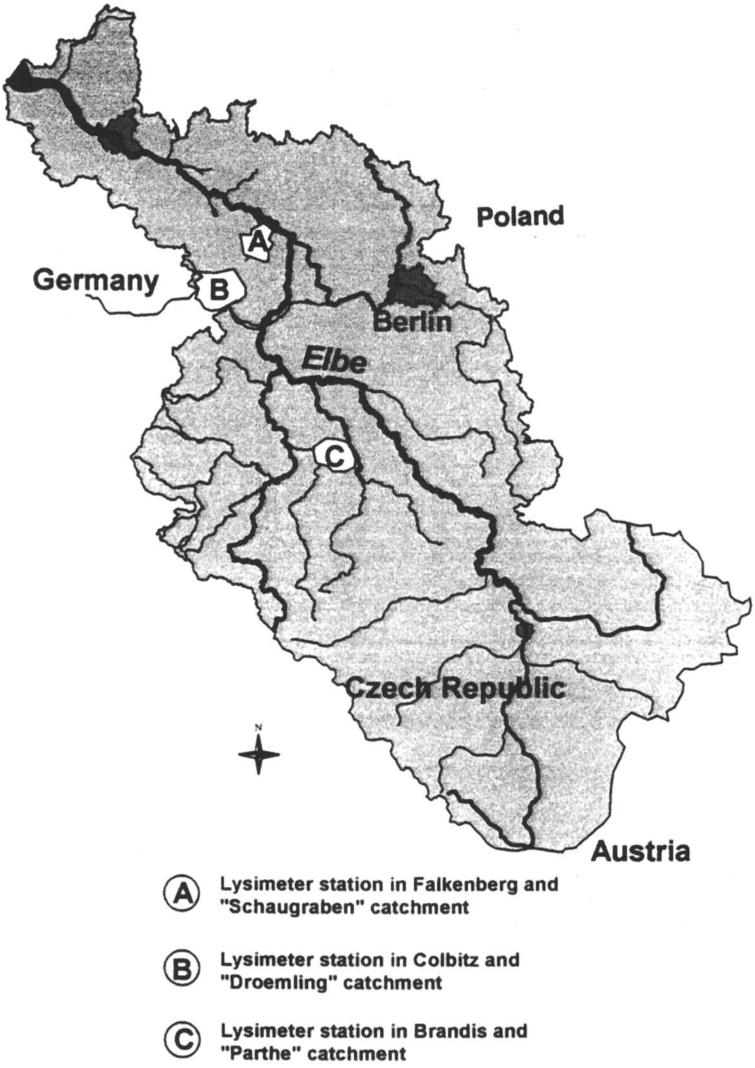
Poland
Germany
A
B
Berlin
Elbe
C
N
Czech Republic
Austria
Ⓐ Lysimeter station in Falkenberg and "Schaugraben" catchment
Ⓑ Lysimeter station in Colbitz and "Droemling" catchment
Ⓒ Lysimeter station in Brandis and "Parthe" catchment

Figure 1. Catchment area of the Elbe river and geographical location of the UFZ managed lysimeter stations and the experimental catchments.

The Station of Small Non-weighable Lysimeters. Twenty non-weighable lysimeters with a surface area of 0.20 m^2, different depths of 0.25 m, 0.5 m, 1.0 m, 2.0 m, 3.0 m and free drainage were filled with sandy and loamy soil profiles in 1989. In November 1995 an experiment was set up to investigate the behavior of different tracers (Cl, Br, D2O, ^{15}N) in soils *(4)* and the leaching of hazardous organic substances (e.g. hexachlorocyclohexane, methoxychlor) commonly found in riverside areas of the former East German chemical industry. The lysimeters were closed on top to exclude plant growth and plant uptake as well as evaporation. Precipitation is simulated by irrigation.

The drainage water from each lysimeter is collected in a separate storage container. At least once a month, the volume of water leached is measured and samples analyzed chemically.

The Lysimeter Stations in Colbitz. There are 2 lysimeter stations in the village of Colbitz representing a forest and a heathland commonly found in the middle of East Germany.

The Non-weighable Lysimeter Station. One non-weighable lysimeter with a surface area of 660 m^2, a total depth of 4.0 m and free drainage was filled with a sandy soil from a forested area and planted with pine trees in 1973. The main objective of this experiment is to quantify the influence of atmospheric deposition and different types of forestry management on the water and solute balance *(5)*.

Three times a month the volume of drainage water is measured and samples are taken for chemical analysis.

The Weighable Lysimeter Station. The 12 monolithic and weighable lysimeters with a surface area of 1.0 m^2, a total depth of 2.0 m and free drainage were filled with heathland soil profiles of the area and planted with different types of heathland vegetation in 1968. The main objective of this experiment is to quantify the influence of different heathland management systems on the water and solute balance *(6)*.

The amount of drainage water and the evapotranspiration is measured daily. At least once a month a sample is taken from each container for chemical analysis.

The Lysimeter Station in Brandis. The 2 lysimeter stations in the village of Brandis near the city of Leipzig represent the area of low precipitation (< 500 mm annually) in middle Germany.

The Weighable Lysimeter Station. The 24 monolithic and weighable lysimeters have a surface area of 1.0 m^2, a total depth of 3.0 m and free drainage. Twenty-one monoliths represent agricultural soil profiles of the area. Three monoliths were sampled from an open-pit brown coal mining area near Leipzig.

The Non-weighable Lysimeter Station. The 19 monolithic and non-weighable lysimeters with a surface area of 1.0 m^2, a total depth of 2.0 to 2.2 m and free drainage were filled with representative agricultural soil profiles of the region. The lysimeter experiments of both stations were set up in 1980 to investigate the influence of agricultural management practices and ecological forms of land use (extensification - without application of fertilizer) on the water balance, the leaching of nutrients and heavy metals, and the production of trace gases *(7)*.

Every day the amount of drainage water and the evapotranspiration (for the weighable lysimeters only) is measured. At least once a month a sample from each lysimeter is taken for chemical analysis.

Experimental Catchment Areas. All lysimeter experiments are linked to representative experimental catchment areas in the field to establish and verify extrapolation domains.

The "Schaugraben" Catchment. Lysimeter experiments in Falkenberg are mainly linked to the "Schaugraben" catchment (about 2,500 ha). The "Schaugraben" is a tributary of the river Elbe in north-east Germany. The "Schaugraben" lowland provides a good example of the change from former socialist co-operative to private farming.

The "Droemling" Catchment. The lysimeter station in Colbitz is linked to the Colbitz-Letzlinger heathland within the "Droemling" catchment (about 55,000 ha) which is the main ground water recharge area for the water supply of Magdeburg, the capital of Saxony-Anhalt.

The "Parthe" Catchment. The lysimeter station in Brandis is located in the "Parthe" catchment (about 36,000 ha) near Leipzig which is mainly urban.

Results of Lysimeter Experiments and Scaling-up

From the various lysimeter experiments the results of the one on effects of land use change on drainage water quality in the "Schaugraben" catchment can be taken as an example.

For this experiment 30 lysimeters filled with sandy loam and previously cultivated intensively are treated in 2 replications as follows:

- 10 lysimeters with a permanent fallow (beginning on August 1, 1991);
- 10 lysimeters with a rotation fallow for one year (the first fallow period was implemented from August 1, 1991 to July 31, 1992) before resuming intensive crop cultivation;
- 10 lysimeters are treated according to BMP (best management practices, whereby fertilization and irrigation is performed in accordance with plant requirements for nutrients and water and with ecological and economical demands).

The lysimeter experiments showed that introducing a long- term fallow (five years) or a rotation fallow for one year to a continuously intensively farmed land results in measurable changes in the water and solute balance within a short time *(8)*. In the fallow treatments deep percolation increases and plant nutrient uptake decreases. Hence, in the first year of fallow the leaching of cations and anions increases compared to intensively cropped plots (Figure 2 a). Leaching of calcium, magnesium and potassium is reduced in the second year (Figure 2 b). In the third year, deep percolation and cation leaching increased in all plots irrespective of cultivation and fertilization practices because the precipitation was 53 % more than average (Figure 2 c). Because of the former intensive cultivation the base saturation of the soils is obviously sufficient to release considerable amounts of cations with increasing volumes of drainage water. In the fourth year, the long-fallow showed slightly, but not significantly, more deep percolation but with reduced leaching of cations and anions (Figure 2 d).

No significant changes in the leaching of phosphorus were detected in fallow treatments because of its firm bonding with soil colloids are unlikely, at least not in the short run. Water bodies are faced with a latent risk of phosphorus accumulation, particularly in areas with sandy soils where mineral and organic fertilizers such as liquid manure, sewage sludge and composted bio-wastes are applied (9).

Leaching of chloride and sulfate became significantly less in the long-term fallow treatment from the second year onward irrespective of changes in deep percolation. Without fertilization or irrigation, the soils are insignificant sources for leaching chloride and sulfate. Anion leaching increases highly when intensive cultivation resumes after the rotation fallow.

No significant difference was detected among the treatments with respect to nitrate. Cumulative nitrate leaching for the four-year monitoring period was highest in the rotation fallow. Compared with lysimeters treated according to BMP, nitrate leaching in the year of set aside was increased by approximately 55 % and in the year of resuming intensive agricultural production by 30 %.

Application of Lysimeter Results to the Experimental “Schaugraben“ Catchment

In order to predict the effects of land use changes on N-losses from the soil and N-loads of the stream for the catchment area of the “Schaugraben“ we applied and verified the results of the lysimeter experiments in the field. The field experiment concerns the “Schaugraben“ catchment, which is about 15 km away from the lysimeter station at Falkenberg (Figure 3), has loamy soils and similar meteorological conditions. Agriculture (61 % arable land; 21.5 % pasture) is the main land use in the catchment. At the headwaters 15.3 % of the area is covered with forest. Historic and recent land use patterns (i.e., forest, pasture, and cropped land including various types of crops and fertilizer regimes) in the “Schaugraben“ catchment have been recorded since 1990 and mapped in a GIS. The catchment area was subdivided into 4 sections (subcatchments). Four gauging stations were set up and discharge and water

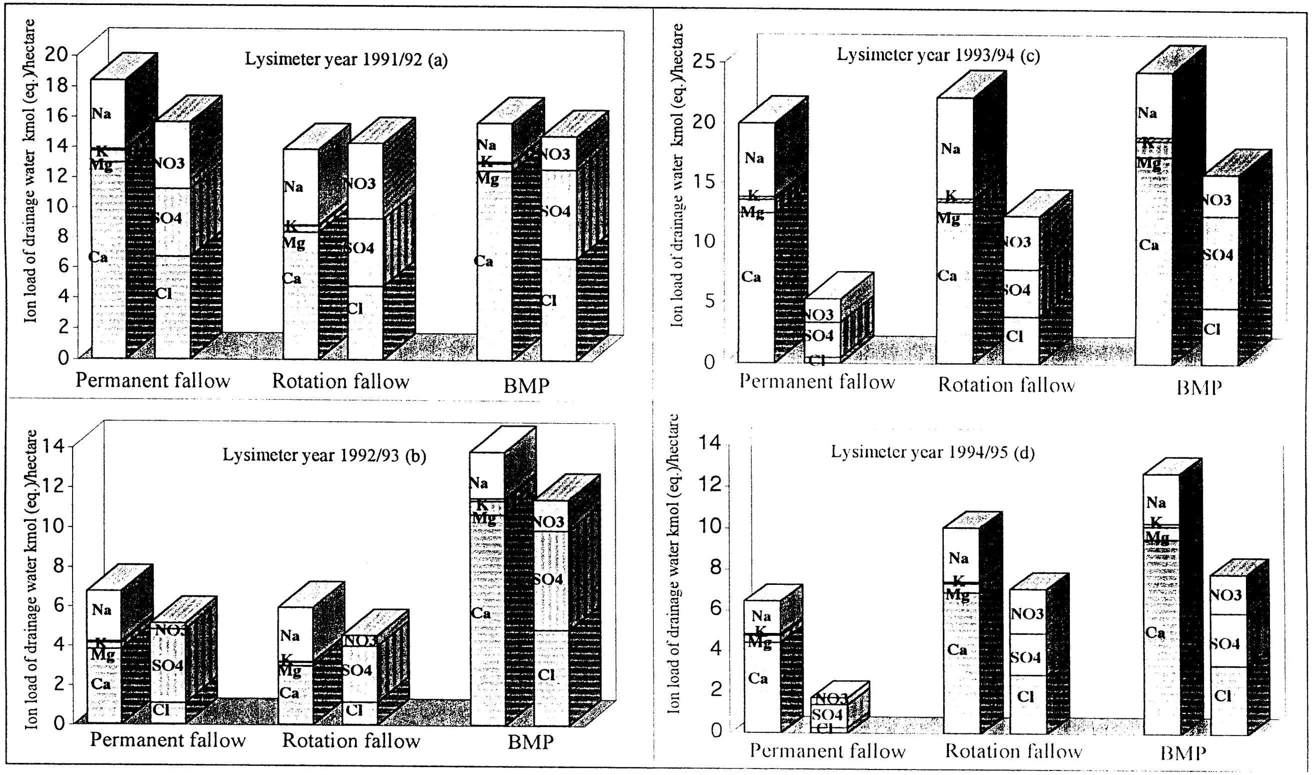

Figure 2. Comparison of ion balances between three different systems of agricultural land management.

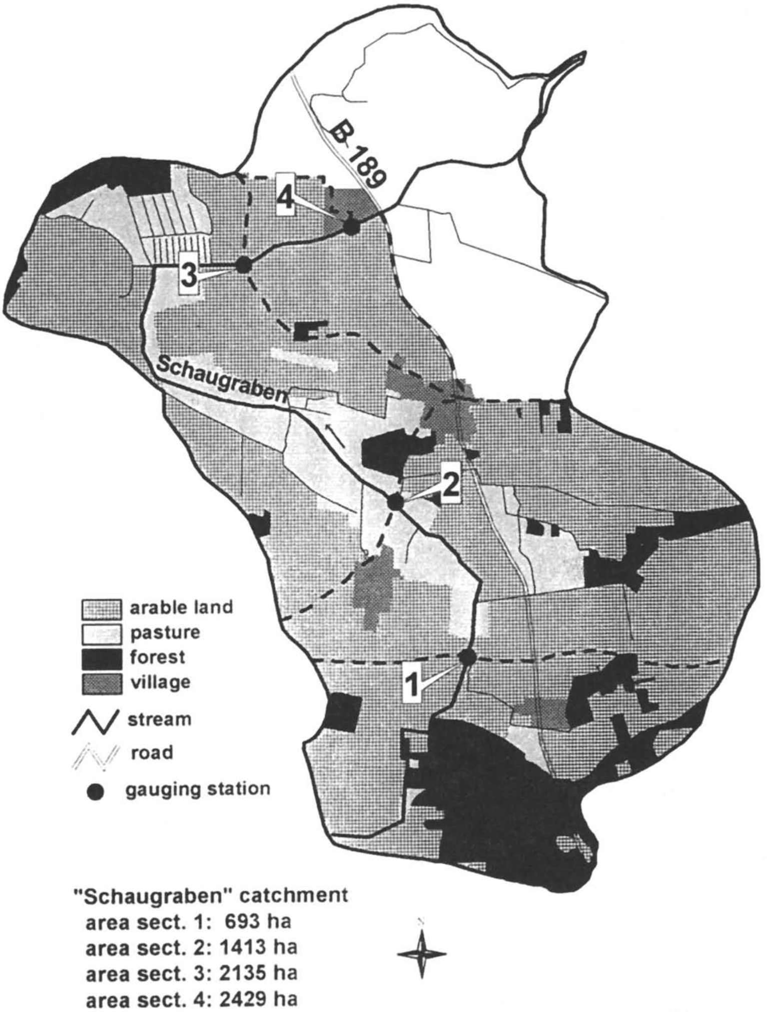
B 189
4
3
Schaugraben
2
1
arable land
pasture
forest
village
stream
road
gauging station
"Schaugraben" catchment
area sect. 1: 693 ha
area sect. 2: 1413 ha
area sect. 3: 2135 ha
area sect. 4: 2429 ha
N

Figure 3. Experimental catchment "Schaugraben" with its subcatchments and land use patterns.

quality have been measured every two weeks since October 1992. In 1996 two sets of ground water wells were installed to determine the flow and quality of ground water. At the outlet of the “Schaugraben“ stream (subcatchment 4) discharge and water quality has been monitored automatically since May 1997.

To extrapolate the results of the lysimeter experiments, the amount of seepage water measured in the lysimeters has to match the ground water recharge in the catchment which was a) calculated according to equations commonly used in Germany and b) the discharge measured in the field (in the northern region of East Germany the ground water recharge is about equivalent to the discharge, to which surface water contributes very little) *(10)*. The more accurate the estimate of ground water recharge, the better is the assessment of the leaching of nutrients from the unsaturated zone.

The quantities of drainage water determined in the long-time lysimeter studies fell within the range of the calculated mean annual ground water recharge rates (Table I).

TABLE I. Comparison of results from long-time lysimeter studies with calculated mean annual ground water recharge in the "Schaugraben" catchment

Reference	*Arable land*** (14.83 km²)*	*Pasture*** (5.23 km²)*	*Forest*** (3.74 km²)*	*Σ Ground water recharge*** (23.80 km²)*
Calculated recharge				
Model "RASTER" *(11)*	-	-	-	125
Bagrov-Glugla* *(12)*	95	- 1	- 1	93
Renger-Wessolek *(13)*	87	15	11	113
Doerhoefer-Josopait *(14)*	96	16	11	123
Long-time lysimeter studies	72	23	2	97

*Long- term mean precipitation at the Falkenberg lysimeter station: 504 mm
Long- term mean evaporation rate at the Falkenberg lysimeter station: 565 mm

** Ground water recharge in mm

Comparing the amount of drainage water measured in the lysimeters and the discharge measured by the State Environmental Protection Agency in Magdeburg in this region during 1993 and 1994 revealed a better match than results of mean annual ground water recharge models commonly used for water management in Germany (Table II). Being located in the region our lysimeters are exposed to the same meteorological conditions while long-time ground water recharge models are not sensitive to short-term variations of meteorological parameters.

The drainage water quantities determined with the lysimeters fall within the variation of ground water recharge rates calculated according to equations commonly used in hydrology. They also comparable to the discharge measured in the field. Therefore, we assume that leaching of nutrients measured with the lysimeters reflects the conditions in the catchment area with sufficient accuracy for extrapolation.

Table II. Comparison of ground water recharge rates in lysimeters and measured discharges in the "Schaugraben" catchment

	Lysimeter data	*Measured discharge*
	1993	
Subcatchment 1	42 mm	55 mm
Subcatchment 2	62 mm	77 mm
Subcatchment 3	63 mm	71 mm
Subcatchment 4	70 mm	85 mm
	1994	
Subcatchment 1	261 mm	343 mm
Subcatchment 2	284 mm	298 mm
Subcatchment 3	285 mm	367 mm
Subcatchment 4	310 mm	422 mm

Determination of N-loss from the Soil. The type of land use is an important consideration when attempting to quantify and predict nitrate leaching and has been surveyed in the experimental catchment every year since 1990 (Table III).

Table III. Cropping systems (% of arable land) in the "Schaugraben" catchment between 1990 and 1995

	Beginning of land use change in 1990	*Current land use in 1995*
Cereals, rape seed	52	55
Corn	7	16
Potatoes	15	6
Sugar beets	9	8
One year rotation fallow	4	11
Other plants	13	4

Based on annual results of the lysimeter studies (N leached in drainage water) and the actual land use in the catchment (crops planted, fallow, pasture, forest) an estimation of N-loss from the soil was made for each year (Table IV).

Table IV. Estimated N-loss of the "Schaugraben" catchment based on lysimeter data for the year 1993

"Schaugraben" catchment		*Lysimeter experiments*			*N-loss*
Land use	*Area*	*Seepage water*	*N-concentration*	*N-leaching*	*from the soil*
	ha	*mm*	*mg/l*	*kg/ha*	*kg*
Cereal	1,038	65	46	30	31,140
Corn	149	71	49	35	5,215
Potatoes	118	132	41	54	6,372
Sugar beets	60	82	34	28	1,680
Rotation fallow	118	80	75	60	7,080
Pasture	523	55	22	12	6,276
Forest	372	0	0	0	0
Σ					**57,763**

Determination of N-load of the Stream. Based on the discharge measured at 4 gauging stations and analysis of its N-content, the annual N-load was calculated for the whole "Schaugraben" catchment and each subcatchment since 1993 (Table V).

Table V. Calculated N-load of the "Schaugraben" stream based on measured data for the year 1993

	Measured discharge	*Mean N-concentration*	*N-load from the stream*
	Tm³	*mg/l*	*kg*
Gauging station 1	149	30	4,500
Gauging station 2	1,002	14	14,127
Gauging station 3	1,538	12	18,416
Gauging station 4	2,236	12	**26,612**

Comparison between N-loss from the Soil and N-load of the Stream. The N-loss from the soil and N-load of the stream at the bottom of the catchment reveal a difference of 30,721 kg/year N and 32,993 kg/year N for the hydrological cycle November to October in 1993 and 1995, respectively (Figure 4).

The most important reason for these differences is probably the highly variable hydrological regime. At present the whereabouts of these amounts of N

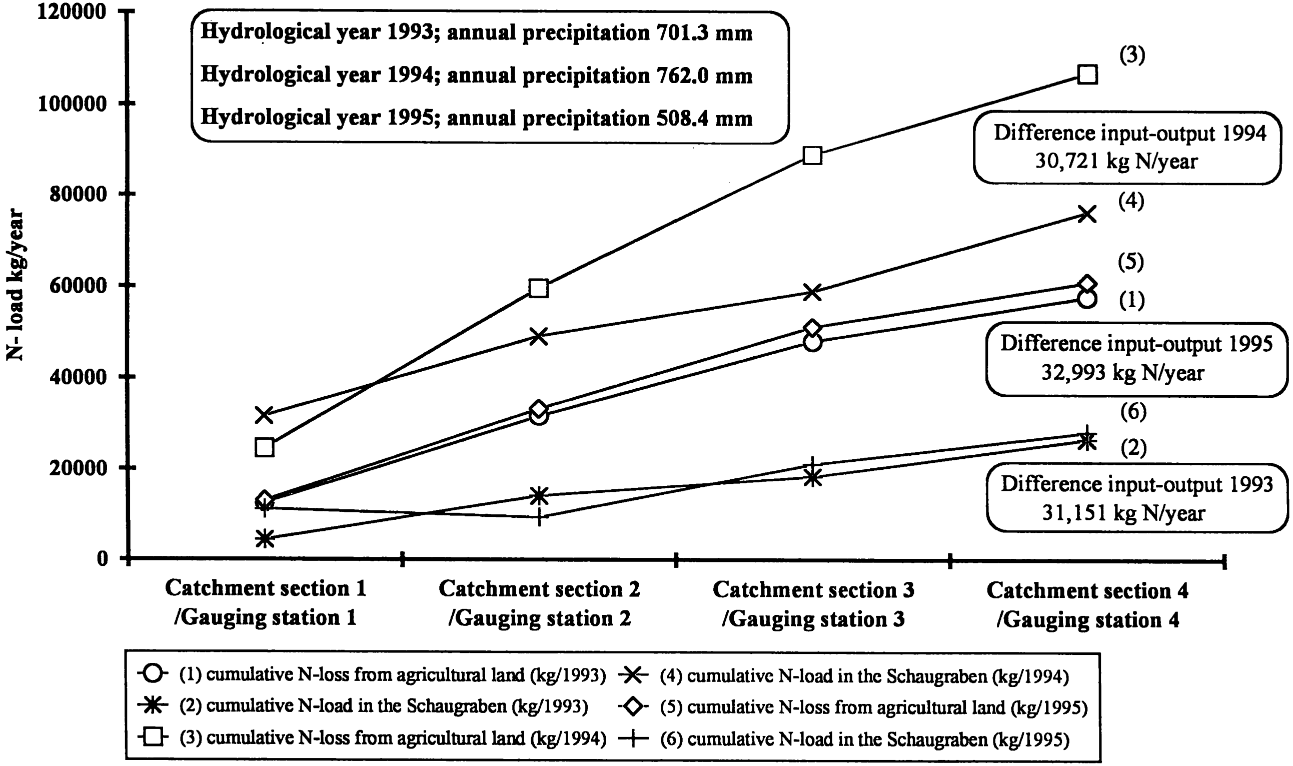

Figure 4. Comparison of the N-loss and N-load for the partial subcatchment areas of the "Schaugraben" stream.

cannot be determined precisely. The observed reductions of 29 and 54 % agree reasonably with postulated factors in the literature *(15)*.

On the basis of above findings we estimated the effect of different fallow systems on the nitrate load of the "Schaugraben". An increase in the proportion of rotation fallow from 10 to 25 % would have raised the N-load of the "Schaugraben" stream by about 10 % during the investigation. However, from the point of view of protecting drinking water quality, rotation fallow is not recommended because of the resulting intensified leaching of nitrates.

Plans for Future Work

To improve the research program we will continuously measure the discharge and water quality at the outlet of the stream. Linking the lysimeter data with GIS data of land use patterns based on remote sensing a more realistic calculation of non-point nutrient input and output on the catchment scale is feasible. In fall 1997 we will start experiments with conservative tracers (Cl or Br), stable isotopes (^{15}N, D2O) and natural isotope signatures (^{2}H, ^{18}O, ^{15}N, ^{34}S) to explore the pathways and transformations of N during transport from the soil surface via the ground water to the surface water. Subject to the availability of resources and progress in quantifying processes as well as calibrating and adapting models (combination of CANDY for the unsaturated zone *(16)* and FEFLOW for the saturated zone (*17*)) we shall attempt to carry out these experiments at both the lysimeter and catchment area levels.

Conclusions

In Germany lysimeters are traditional instruments for measuring the amount of drainage water and studying the behavior of chemical substances during their transport through the unsaturated zone.

The different types of lysimeters available allow a realistic simulation of a wide range of scientific and practical questions on the small and medium scale. If sufficient lysimeters are available for the experimental replications needed, lysimeters are ideal research facilities to explore environmental impacts of land management, to develop and test simulation models and to design sound and feasible management practices. Much of the needed information can be collected faster compared to field or catchment studies, which however remain essential for the ultimate validation of results. A limiting factor of lysimeter studies is often the insufficient number of replicates required to handle the variability of parameters.

Acknowledgments

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Chapter 13

Soil-Bound Residues

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Long-term outdoor lysimeter studies using ^{14}C-labelled compounds allow the quantification of the 'soil-bound residue fraction'. Referring to more than twenty lysimeter studies under realistic environmental conditions, it can be concluded that more than 80 % of residual carbon of the molecule is retained in the top soil layer even after several years. Usually 50 to 90 % of this residual radiocarbon can be considered to be a 'soil bound residue' once the chemical structure has been clarified. The high amount of microbial biomass in the topsoil continuously influences the chemical and biochemical metabolism of pesticide molecules interacting directly with the total soil organic matter turnover. The combined use of e.g. ^{14}C, ^{13}C and ^{12}C labelling techniques offers the opportunity to characterize the nature of these residues in the humus matrix. For instance NMR spectroscopy assists in detection of molecules bonding in the humus matrix by both enrichment of the test compound with ^{13}C and depletion of ^{13}C in the organic matter of an artificially produced soil. Aspects of bioaccessibility and/or bioavailability as well as the environmental relevance of these residues will be addressed. Important conclusions of a workshop on bound residues organized on behalf of the German Research Foundation in 1996 will also be presented.

'Non-extractable residues (occasionally referred to as „bound residues") in soil are chemical species (active ingredient, metabolites and fragments) originating from pesticides, used according to good agricultural practice, that are unextracted by methods which do not significantly change the chemical nature of these residues, but which remain in the soil. These non-extractable residues are considered to exclude fragments recycled through metabolic pathways leading to naturally occurring products.' This is the wording of the definition according to the International Union of Pure and Applied Chemistry (IUPAC), as cited by the Applied Chemistry Division, Comission on Pesticide Chemistry (*1-3*). Calderbank (*4*) modified the definition with special emphasis on the aspect of bioavailability. He stated: '...Clearly the important matter is not so much how the residue is defined but the question of its biological availability.' Carry-over into succeeding crops causing phytotoxicity problems, leaching to groundwater and potential long-term effects on soil quality are his concerns.

What is generally assumed today is that the active ingredients of pesticides cannot be liberated from the bound residue fraction in appreciable amounts. Reduced mobility and biocidal activity due to bonding to humic substances are often described (*5-8*). It is in some cases supported by various experimental results, that parent molecules or metabolites are bound to the humic matrix either by covalent bonding (*9-16, 51*), ionic bonding (*17-28*), charge transfer complexes (*29-33*), ligand exchange (*34,35*), hydrogen bonding (*23, 31, 36-40*), van der Waals forces (*22, 41-44*), hydrophobic sorption (*45-50*) or entrapment due to sequestration reactions (*52*).

Lysimeter Studies in Soil Bound Residue Research

In general microbially and physico-chemically induced processes are responsible for the formation of bound residues. Important parameters influencing the fate of organic chemicals in soil are temperature, humidity and aeration as climatic factors and texture, organic matter, microbial biomass, biological diversity as well as plant cover as soil characteristics (*53*). Especially organic matter constituents play a decisive role as reaction partners in this respect. Most of these parameters undergo season-dependent variations with clear effects on the turnover of a chemical. It is rather difficult to include all possible scenarios in experiments. Outdoor lysimeter studies with ^{14}C-labelled pesticides come close to reality (*54-58*). Referring to lysimeter studies at the Institute of Radioagronomy, it can be concluded that more than 80 % of residual carbon of a molecule is retained in the top soil layer even after several years (Table I). Usually 50 to 90 % of this residual radiocarbon can be considered to be a 'soil bound residue' because this fraction is not extractable by exhaustive extractions with organic solvents. Nevertheless, in many cases the nature of the soil bound residue has not been clarified yet.

The high amount of microbial biomass in the topsoil continuously influences the chemical and biochemical metabolism of pesticide molecules interacting directly with the total soil organic matter turnover. It has to be considered that approximately 2-3 kg C as part of pesticide molecules applied to one ha of farm land (moderate climatic zone, Western Europe) are drawn into the organic carbon cycle of the plough layer (Figure 1). In total about 8 t of organic carbons are metabolized and rearranged dynamically with peaks of metabolism during the growing season. The most important end product of the metabolism is CO_2 (*2, 65-70*) which is released from the soil system. This underlines that we are dealing with an extremely wide ratio between carbon-structures originating from pesticide molecules and those from natural sources (soil organic matter, plant residues, soil microbial biomass, organic manure).

Table I. Outdoor Lysimeter Studies with Undisturbed Soil Columns (1.1 m Depth) in the Institute of Radioagronomy: Balance of Radioactivity

Applied radioactivity = 100 %

			Radioactivity detected in		
Compound/Ref.No.	*Soil type*	*Years of study*	*Total core 0-110 cm %*	*Top soil 0-30 cm %*	*Bound residues 0-30 cm %*
Atrazine (*59*)	Ol^a	2	41.1	35.7	23.9
	GC^b	2	33.6	29.7	21.1
Terbuthylazine (*60*)	OL	2	66.5	57.1	37.9
	GC	2	64.0	56.1	35.4
Chloridazon (*61*)	OL	2	76.7	68.1	45.7
	GC	2	64.4	44.4	33.1
Dichlorprop-P (*61*)	OL	2	19.3	19.1	18.4
	GC	2	27.4	27.1	26.4
Methabenzthiazuron (*62*)	OL	2	79.8	79.2	47.5
	OL	6.5	20.2	19.1	17.1
Pyridate (*63*)	OL	2	46.0	45.2	38.5
Anilazine (*64*)	OL	9	84.0	82.0	64.3

OL^a: orthic luvisol 1.2 % C_{org}, 6.4 % sand, 78.2 % silt, 15.4 % clay, pH 7.2 in top soil layer, GC^b gleyic cambisol 0.9 % C_{org}, 74.1 % sand, 21.7 % silt, 4.2 % clay, pH 6.9 in top soil layer.

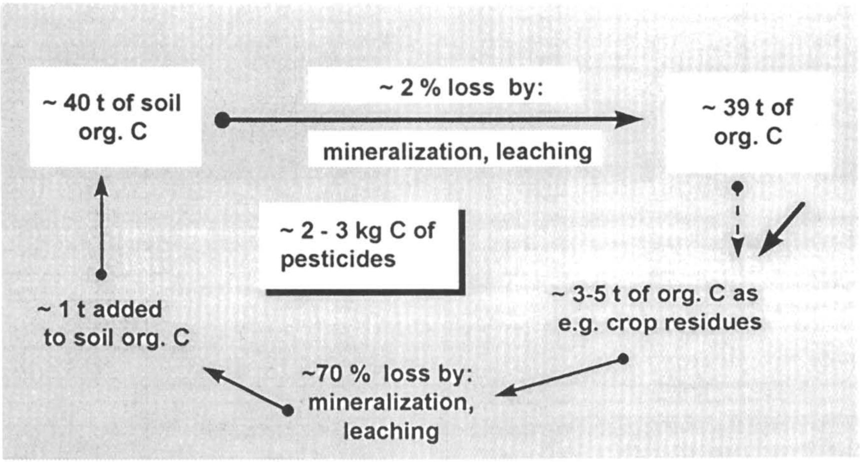
~ 40 t of soil org. C
~ 2 % loss by:
mineralization, leaching
~ 39 t of org. C
~ 2 - 3 kg C of pesticides
~ 1 t added to soil org. C
~ 3-5 t of org. C as e.g. crop residues
~70 % loss by: mineralization, leaching

Figure 1. Average organic carbon balance of a plough layer.
Assumptions: moderate climate, one year of observation, one ha, 4000 t of soil (0-30 cm depth), 1% of organic carbon.

Characterization of the Soil Bound Residue Fraction. In a long-term lysimeter study with an undisturbed profile of an agriculturally used degraded loess soil (orthic luvisol), the herbicide [carbonyl-^{14}C] methabenzthiazuron was applied postemergent to winter wheat at a rate of 2.8 kg a.i. ha^{-1}. At harvest, 127 days after application, the amount of unchanged compound in the extracts of organic solvents was 28.8 % of applied methabenzthiazuron, coinciding with a severe reduction in the extractable and potentially bioavailable portion of residual radioactivity (Figure 2). In November 1990, 6.5 years after the application, an amount of less than 1 % was characterized as methabenzthiazuron in the organic solvent extracts. From fulvic and humic acid fractions as part of the soil bound residue fraction, trace amounts of parent compound (less than 0.05 % of applied rate) could be reextracted with chloroform. The continuous reduction of the total residues during the long-term experiment proves that the bound residue fraction of methabenzthiazuron is slowly metabolized in parallel to the turnover of natural organic carbon fractions in soil, supported by the finding that less than 1 % of the applied radioactivity could be detected in the soil microbial biomass of the total soil core (*71*).

The bioavailability of the carbonyl-carbon of the urea side-chain of methabenzthiazuron to the succeeding rotational crops was drastically reduced (winter wheat 2 % , winter barley 0.2 %, sugar beets 0.012 %, winter wheat 0.017 % and winter barley 0.006 % of applied radioactivity) due to binding/fixation or sequestration processes (*52*, *62*). Some of this radiocarbon in the plants may even result from assimilation of the mineralization end product $^{14}CO_2$, as was demonstrated with [3-^{14}C] metamitron in a lysimeter study (*72*).

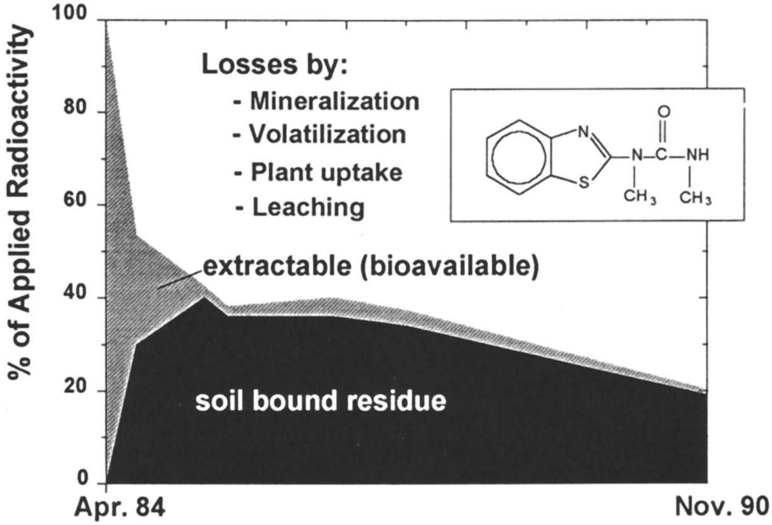

Figure 2. Lysimeter experiment with [carbonyl-^{14}C] methabenzthiazuron: Distribution of residual radioactivity in the soil.

Applied Radioactivity = 100 %.

The fungicide anilazine is known to generate high amounts of soil bound residues very rapidly coinciding with a low rate of biomineralization of less than 2 % in twelve weeks, regardless of the concentration range of 1-400 mg kg^{-1} of soil used in laboratory scale degradation experiments (*73-76*). In order to evaluate binding and bioavailability under realistic conditions a long-term lysimeter study with an undisturbed profile of an agriculturally used degraded loess soil (orthic luvisol) was performed. In 1985 [phenyl-U-^{14}C] anilazine was applied postemergence to winter wheat at a rate of 4 kg a.i. ha^{-1}, followed by four repeated applications at the same rate in the years 1986 through 1989. The application of the compound at such high concentrations onto the soil surface was performed to study binding in soil and bioavailability for plants in detail. The application was not in accordance to good agricultural practice. As shown in Figure 3, the ratio between the extractable portion and the soil bound fraction is almost the same regardless of the experimental design. On the basis of this result specially designed laboratory experiments were carried out to characterize the binding mechanisms of anilazine in the soil matrix, e.g. the humic acid fractions of the orthic luvisol.

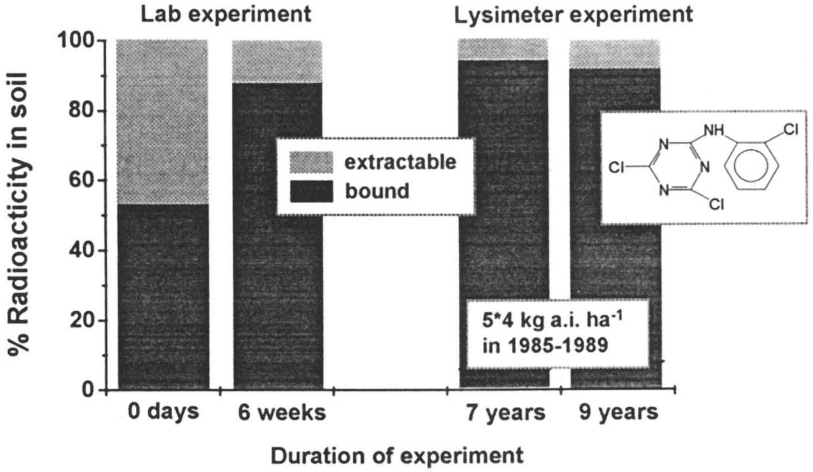

Figure 3. Extractability of [phenyl-U-^{14}C] anilazine from soil samples of an orthic luvisol. Radioactivity in the soil sample = 100 %.

^{13}C-NMR Measurements. In this respect ^{13}C-nuclear magnetic resonance spectroscopy (NMR) offered a possibility to observe the chemical nature of the bound residue in the humic acids of incubated soil samples. As a prerequisite it was on one hand necessary to enrich those carbon atoms of anilazine responsible for the bondings by selective synthesis with ^{13}C-isotope. This caused clear signals above those of the humic acids background in the NMR measurement (*76*). On the other hand an artificial soil (A-soil) was employed with humic substances derived from a humified ^{13}C depleted corn straw in a previously calcined soil matrix (*77*). This led to lower background signals of the NMR spectra of the humic acids.

^{13}C-NMR measurements of organic samples dissolved in $CDCl_3$ were carried out by proton noise decoupling with $CDCl_3$ as internal standard. The humic acids were measured in 0.5 M deuterated sodium hydroxide solution by inverse gated decoupling with dioxane as external standard (*78*). Both experiments were carried out using either an AC 200 Bruker (50.3 MHz) or an AMX 400 Bruker (100.6 MHz) NMR spectrometer. The conditions of the NMR measurements are shown in Table II.

Table II. Conditions of ^{13}C-NMR Measurements

Experiment	*Proton noise decoupling*	*Inverse gated decoupling*
Acquisition / s	1.0	0.172
Pulse width / °	30	45
Relaxation delay / s	0.5	1.0
Decoupler	on	off, during relaxation
Line broadening / Hz	1 - 2	8 - 40
Number of scans	ca. 40.000	100.000 - 190.000
Solvent	$CDCl_3$	0.5 *M* NaOD
Standard (with respect to TMS)	$CDCl_3$, intern, $\delta = 77.05$ ppm	Dioxane, external, $\delta = 67.4$ ppm

Anilazine was available as [triazine-U-^{13}C]anilazine, 90-99 % ^{13}C-enriched. As NMR standard substances for the detection of the chemical shifts, the dihydroxy derivate (2-chlorophenyl-dihydroxy-(1,3,5)-triazine-2-yl-amine) and the dimethoxy derivate (2-chlorophenyl-dimethoxy-(1,3,5)-triazine-2-yl-amine) were used. The NMR spectra of the reference compounds are shown in Figure 4.

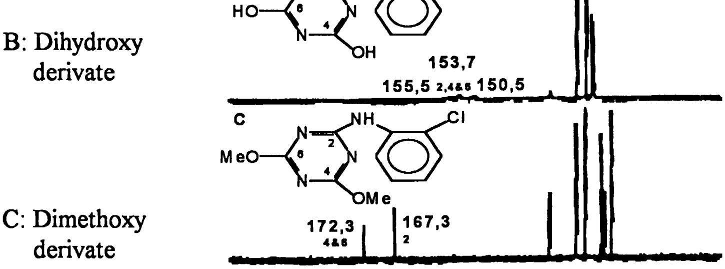

Figure 4. Structural formula and NMR spectra of reference compounds without ^{13}C enrichment. (Adapted from ref. 76)

Figure 5 exhibits the NMR spectra of native humic acids and humic acids of the artificial soil originating from the incubation of calcined soil with corn straw (90 % calcined mixed with 10 % fresh soil as an inoculum for the turnover of the straw). After Wilson (*79*) the spectra can be divided into four regions: aliphatic region δ = 0-46 ppm, C-O/C-N region δ = 46-110 ppm, aromatic region δ = 110-160 ppm and carboxyl and carbonyl group region δ = 160-220 ppm. It is obvious that the strucure of native humic acids and the humic acids originating from the humification of corn straw with natural ^{13}C abundance are almost identical. Signals of humic acids from ^{13}C-depleted corn straw (five-fold enlargement) are significantly reduced. This result shows that it is possible to produce humic acids similar to native humic acids from soil (77).

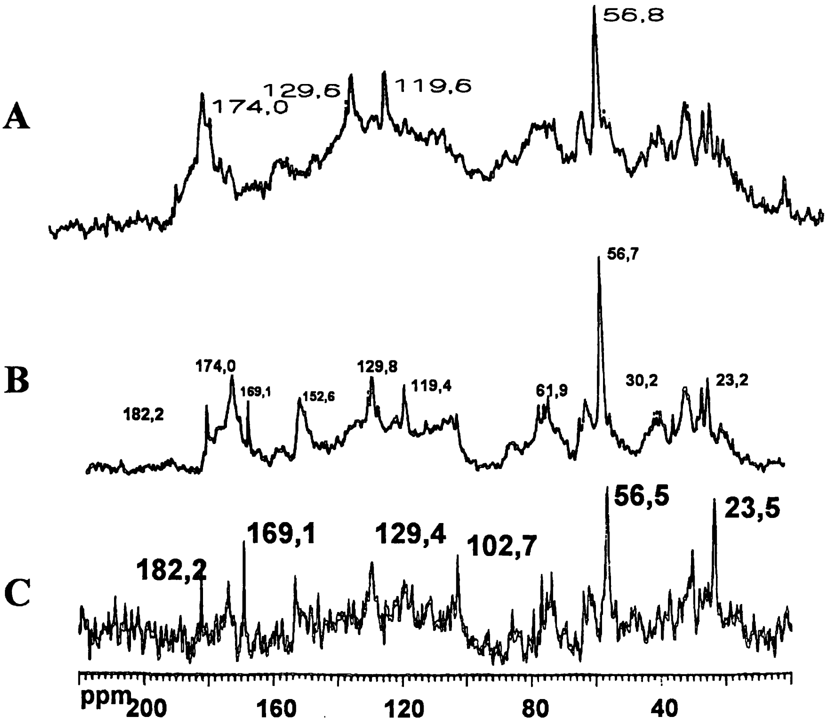

Figure 5. ^{13}C NMR spectra of humic acids: A: humic acids of the orthic luvisol top soil layer; B: humic acids after corn-straw humification with natural isotope ratio (90/10), C: humic acids after ^{13}C-depleted corn-straw humification (90/10) five-fold enlarged. The spectra were normalized according to the signal δ = 57 ppm (O-CH_3-groups of lignin). (Adapted from ref. 77)

Figure 6 exhibits the results of the incubation of [triazine-U-^{13}C]anilazine in different soils. Soil samples were incubated in portions of 100 g of soil in Erlenmeyer-flasks at 20 to 25 °C and 60 % of the maximum water holding capacity for at least six weeks. After the incubation the soil samples were extracted with organic solvents followed by an extraction with 0.5 M sodium hydroxide solution and separated by centrifugation. The supernatant was acidified with 0.1 M hydrochloric acid to pH < 2. The precipitated humic acids were separated by centrifugation and redissolved in sodium hydroxide solution (0.5 M), dialysed against distilled water and prepared for NMR measurements (*76, 77*).

All spectra can be characterized by clear signals at δ = 166.4 - 166.9 ppm and δ = 172.0 - 172.8 ppm which corresponds to the chemical shifts of the dimethoxy derivate of anilazine (Figure 4). In general, signals of the dialkoxy bonding to the humic matrix are better at concentrations of 400 mg kg^{-1}. The advantage in using the artificial soil (A-soil) is the very low background of the spectrum which results in more distinct signals of the ^{13}C-enriched triazine ring carbons at a lower concentration of anilazine of 50 mg kg^{-1}. The chemical shifts of anilazine and its dimethoxy derivate (as a reference for the dialkoxy-bonding of anilazine to the humic matrix) are fairly close together (Figure 4). But it was shown that free parent compound could not be detected in humic acids as well as fulvic acids (*76, 80*). In conclusion, this is an example of a covalent bond of a pesticide molecule in a specific fraction of the soil organic matter. The same type of covalent bond of anilazine was also found in a sandy soil (*76, 81*).

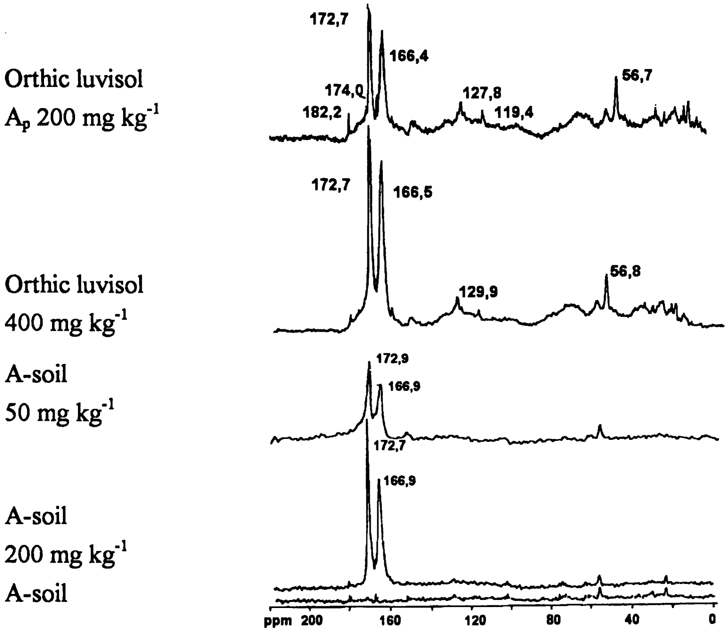

Figure 6. ^{13}C NMR spectra of humic acids from an orthic luvisol and an artificial soil (A-soil) incubated with 50 - 400 mg kg^{-1} [triazine-U-^{13}C] anilazine: δ 166.4-166.9 ppm C-atoms of aniline-bridges of the triazine-ring; δ 172.0-172.8 ppm other C-atoms of the triazine-ring.
(Adapted from ref. 81)

Bioavailability of humic acid bound fragments of anilazine tested in liquid cultures with soil microorganisms is negligible (*80*). Results from the lysimeter study support low rates of bioavailability also for succeeding rotational crops. Less than 0.3 % of applied radioactivity was taken up by winter barley one year after the annual applications of anilazine for five consecutive years. Four years after the last application the amount of radioactivity in winter wheat originating from the [phenyl-U-^{14}C] label of anilazine was reduced to less than 0.01 % (64). Nevertheless, as with other tested compounds, assimilation of released $^{14}CO_2$ by the plant cover must be considered, too (*72*).

Conclusion and Research Options

The information that has been presented shows that lysimeter experiments with radiolabelled compounds yield information on the general situation of bound residue formation dependent on all abiotic and biotic natural parameters. The experiments are embedded in a system of good agricultural practice which opens possibilities to describe aspects of potential bioavailability and translocation of soil-water bound residues in the long term view under natural environmental conditions. Soil-water bound residues are formed by the interaction of aquatic humic substances and xenobiotics or their metabolites. On the basis of the results from lysimeter experiments specific laboratory scale studies can be designed to clarify various types of bonding. As recently discussed (*82*), innovatively applied analytical methods like silylation of soil organic matter constituents, solid-phase microextraction, thermodesorption, pyrolysis-GC-MS and sophisticated bioassays will broaden the insight into the field of bound residue research. The combination of analytical approaches with the use of stable and radioactive isotope labelling techniques (^{12}C, ^{13}C, ^{14}C, ^{15}N, ^{31}P) can be extremely advantageous in this respect. In addition, aspects of soil biology in relationship to soil organic matter turnover can be addressed and may contribute to enlarge the knowledge in this field, respectively.

In conclusion of the workshop on bound residues organized on behalf of the German Research Foundation in 1996, an advanced definition of bound residues is proposed: 'Bound residues represent compounds in soil, plant or animal which persist in the matrix in the form of the parent substance or its metabolite(s) after extractions. The extraction method must not substantially change the compounds themselves or the structure of the matrix. The nature of the bond can be clarified in part by matrix-altering extraction methods and sophisticated analytical techniques. To date, for example, covalent, ionic and sorptive bonds as well as entrapments have been identified in this way. In general the formation of bound residues reduces the bioaccessibility and the bioavailability significantly' (*82*).

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Chapter 14

Modeling Water Flow and Pesticide Transport at Lysimeter and Field Scale

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Lysimeters are used in European countries as a final tier for assessing the groundwater contamination potential of pesticides with leaching tendencies. The effect of the artificial lysimeter bottom boundary condition on soil water budget components was investigated with the help of the WAVE model in comparison with data from a lysimeter study after pre-emergence application of [^{14}C]methabenzthiazuron (MBT) conducted over 252 days. Simulated drainage fluxes in the degraded loess soil were larger using a free drainage boundary condition. Furthermore the effect of measured spatial variability of the soil water retention characteristic on simulated water fluxes was investigated with a monte-carlo modelling approach. The predicted variation of leaching volume was considerably larger than observed in five lysimeter replicates. The effect of spatial variability of the sorption distribution coefficient on soil residue profiles was negligible for the herbicide methabenzthiazuron (MBT). In contrast variable soil hydraulic properties did affect the centre of mass of the pesticide residues. Considering the statistical uncertainty of the degradation rate parameter estimation from laboratory data resulted in huge variability of predicted total MBT residues.

Pesticides are widely used to ensure a predictable, reliable and high quality crop production throughout the world. In the 70's and 80's residues were increasingly found in groundwater systems of agroecosystems *(1)*. To protect natural water resources regulatory measures and drinking water standards were initiated by the responsible authorities. In Europe, the 0.1 $\mu g\ L^{-1}$ limit for the presence of pesticides in drinking water was established. Modern risk assessment of potentially hazardous chemicals requires the quantification and prediction of solute transport in soil-aquifer systems.

Although mathematical models are gaining importance in risk assessment of pesticides, experimental studies are still a crucial part of evaluation procedures in dif-

In The Lysimeter Concept; Führ, F., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 1998.

ferent countries. At present there is not a world-wide standard procedure on how to conduct experimental studies in these evaluations. In Germany, e.g., lysimeter studies are the final tier for assessing the groundwater contamination potential of pesticides with leaching tendencies *(2)*. In the United States ground-water monitoring studies are required in this case. Both methods have a fundamentally different approach and philosophy.

Lysimeters have a long and outstanding tradition in the experimental quantification of soil water processes, such as the loss of soil water by evapotranspiration or drainage. A good review of existing lysimeter systems can be found in *(3-4)*. Lysimeters offer an unique possibility to control and measure the components of the water and chemical balances and fluxes in soils. In combination with ^{14}C labelled pesticides *(4)* discuss the use of lysimeters to quantify total pesticide residues in plants, soil and leachate. The greatest advantage of lysimeters lies in the comparison of flux averaged measured and predicted leachates (fluxes of water and solute). The free draining bottom boundary condition, caused by cutting off the soil monolith at a certain depth, might be different from the field situation. Although this does not necessarily limit the appropriateness of lysimeters for modelling purposes, it might limit the direct transfer of information from the lysimeter to the field situation.

Field monitoring studies used in the US for assessing leaching tendencies of pesticides include the characterization of movement and dissipation in the unsaturated zone. Additionally, the behaviour of the pesticide is monitored in groundwater. These monitoring studies consider the effect of spatial variability of soil properties, surface runoff and lateral flow on pesticide behaviour that cannot be accounted for in lysimeter experiments. A detailed discussion covering this topic is given in *(5)*.

Mathematical models provide the possibility to assess and predict the leaching potential of pesticides under various scenarios including different soil types, different crops and management strategies. Combined with Geographical Information Systems a more sophisticated approach to managing the use of pesticides is possible. Recent mathematical models for this purpose frequently assume model parameters to be uniformly distributed at the scale of application. The 1-dimensional models presently discussed in Europe to predict leaching behaviour assume soil properties to be uniformly distributed at the field scale *(6)*. There is, however, abundant evidence in literature that soils vary in space *(7)* and that this variation has an important influence on field scale solute transport *(8)*.

If field soils were uniform in their properties measurements at one location would contain all the information required to make an estimate of e.g. the field scale leaching behaviour. Due to heterogeneity usually a large number of locations and thus measurements is required, the amount being a function of the degree of heterogeneity and the correlation length of soil properties. For simple soil properties such as percentage of sand , bulk density or organic carbon content this is still a feasible procedure. Measurements of more complex parameters like soil hydraulic properties or solute transport parameters are not only expensive but also time consuming. In addition these parameters only provide indirect information on the leaching behaviour at the field scale as they have to be used in mathematical models.

Basically two approaches are presently available to quantify field scale behaviour of solute transport : the use of stochastic flow and transport models or the Transfer Function (TF) or mass solute flux approach. The TF approach formulates the transport process as an integral property of soil which is defined in terms of an experiment. This experiment yields an integral description of the soil which incorporates all heterogeneities that influence the transport process *(9)*. Use of the TF approach requires the experimental characterization of the travel time probability density functions.

Stochastic flow and transport models assume that the parameters needed can be described as random space functions. The characterization of these random space functions is derived from measurements made at various locations within one field site. The usual approach is to assume that these properties are the result of a second order stationary process. Characterization of the spatial variability then requires the mean value, the variance and correlation length of the parameter. If physico-chemical properties tend to be correlated in space cross-covariance functions are also needed. The solution of these stochastic equations with second order stationary parameters requires the use of numerical models. If field scale behaviour is the objective, the full 3D flow and transport equation needs to be solved. Depending on the correlation length of soil properties and the extent of the flow and transport domain, this may result in large numerical problems in terms of the number of grid points. A first approximation of the impact of heterogeneity on solute transport and thus a quantification of field scale leaching behaviour is obtained by neglecting the spatial dependence of properties. This reduces the transport problem to a 1D stochastic problem.

This approach then only requires the mean, variance and the covariance of each of the properties considered. Solution of the stochastic flow and transport equation is obtained using a monte-carlo simulation which involves the repetitive solution of a 1D deterministic problem with varying parameter values according to a specified distribution.

In this paper an analysis of the fate of the herbicide methabenzthiazuron (MBT) in lysimeter studies and a monte-carlo method with a deterministic mechanistic model are presented in order to determine field scale behaviour. Data of five replicate lysimeters (Dust et al., submitted for publication) and results from a field scale study, where variability of several parameters was investigated were used.

Results of the lysimeter study will be discussed in terms of the variability in soil water balance components, total residues and dry matter production. The field scale variability was experimentally determined for the soil hydraulic properties and the sorption distribution coefficient at an 1 ha field site. Variation of the local scale microbial decay parameter was also included.

The WAVE model *(10)* was used to calculate the water flow and transport of MBT under cropped conditions. The calculations will be compared to results obtained with a pure deterministic approach and measurements obtained from lysimeter systems. This includes the analysis of the effect of boundary condition on flow and transport.

Material and Methods

Lysimeter Study. The five outdoor lysimeters with a surface area of 1.0 m^2 and a profile depth of 1.1 m contained an undisturbed degraded loess soil (Orthic Luvisol) with two horizons (Table I). Two lysimeters were treated pre-emergence with [phenyl-ring-^{14}C]MBT to winter wheat at a field-rate of 2.8 kg ha^{-1} formulated as 4 kg TRIBUNIL (registered trade mark Bayer AG) ha^{-1} on November 25, 1988. The lysimeters were monitored for leachate on a three-week basis and analysis for MBT-residues were conducted for the treated lysimeters. Soil samples were taken and analyzed for MBT-residues from the plow layer (0-0.4 m) after harvest of the treated wheat. Soil moisture contents were recorded discontinuously in the entire soil profiles with a neutron probe for the five lysimeters. Measurements were conducted at 0.20, 0.30, 0.45, 0.65 m below soil surface. On the basis of rainfall data, leachate volumes and observed changes in soil water storage calculated from the moisture contents, actual evapotranspiration (ET_{act}) was calculated by difference. Precipitation, air temperature and humidity, and wind velocity were recorded with an automatic weather station.

Table I. Physico-Chemical Soil Characteristics of the Orthic Luvisol.

Soil horizon	A_p, *0-0.4 m*	B_t, *0.4-1.1 m*
Sand (> 63 μm) (%)	6.4	0.5
Silt (2 - 63 μm) (%)	78.2	73.4
Clay (< 2 μm) (%)	15.4	26.1
Bulk density (g/cm^3)	1.57	1.46
C_{org} (%)	1.2	0.3

Field Characterization. The spatial variability of the soil hydraulic properties and the sorption distribution coefficient for MBT was experimentally determined at the field site Merzenhausen. The spatial variability of $h(\theta)$ was determined from 11 samples in the A_p and 46 samples in the B_t horizon. The $h(\theta)$ was described using the Van Genuchten model (equation 6). The soil hydraulic properties were measured using a modified multistep outflow method *(11)*.

The moisture retention characteristic parameters were obtained by fitting the Van Genuchten model to the equilibrium moisture content data at six pressure levels of the outflow measurements. Only α and n were estimated from these data. θ_r was fixed to zero and θ_{sat} was directly calculated from the bulk density (Table II).

To obtain normally distributed parameters α was log transformed and n was transformed using the Johnson transform (Table III)):

$$J(n) = \ln((6-n)/(n-1.05)) \qquad (1)$$

From these data the covariance matrix (CM) was calculated for the A_p and B_t horizon (Table IV). The hydraulic conductivity was described with the Gardner model (equation 7) The parameters were estimated with pedotransfer function presented by *(12)* (Table II).

The spatial variability of the K_d-value was obtained from the spatial variability of the organic carbon content C_{org} (kg kg^{-1}). C_{org} was determined on 120 samples, taken at a regular grid on the Merzenhausen field site at depths between 0 - 0.4 m and 0.4 - 0.6 m. To obtain normally distributed C_{org} values the following Johnson transforms were used:

$$0 - 0.4\,m: \qquad J(C_{org}) = \ln((16 - Corg)/(Corg - 1.11)) \qquad (2)$$

$$0.4 - 0.6\,m: \qquad J(C_{org}) = \ln((13 - Corg)/(Corg - 0.33)) \qquad (3)$$

The mean and variance of $J(C_{org})$ for A_p and B_t were equal to 3.61, 0.364 and 3.59, 0.401 respectively. The generated K_d-values for the monte-carlo simulation were obtained by back transformation and multiplication C_{org} with a K_{oc} factor of 600 (L kg^{-1}) *(13)*.

The variability of the *A* and *B* parameter in the microbial decay model of Walker *(14)*, equation 10 was obtained from lab scale experiments. Degradation studies of MBT were performed on three samples with four moisture levels (20, 40, 60, 90 % of the saturated moisture content). MBT-residue were determined at days 1, 4, 8, 10, 32, 64 and 128 after incubation. Rather than fitting a first order kinetic model to the mean values at the different moisture levels equation 10 was fitted to all the data. The mean and variance of *A* and *B* were found to be equal to 101.6, 1892.25 and 0.053, 0.031, respectively. The value of the covariance was equal to 7.46.

The WAVE Model. The mechanistic-deterministic WAVE model *(10)* was used to quantify the fluxes and state variables of both lysimeter studies. Basically, the one-dimensional model simulates the water flow, solute transport and heat flux under transient conditions in a cropped, vertically layered soil. Water flow is described with the Richards' equation

$$C(h)\frac{\partial h}{\partial t} = \frac{\partial}{\partial z}\left[K(h)\left(\frac{\partial h}{\partial z} + 1\right)\right] + S(h,z) \qquad (4)$$

where h is the pressure head (cm), t is time (day), K(h) the hydraulic conductivity (cm d^{-1}), C(h) the differential moisture capacity (cm^{-1}), z the vertical co-ordinate (cm) and S(h,z) the source-sink term (d^{-1}). Equation 4 is solved numerically using an implicit finite difference scheme with explicit linearization of the hydraulic properties. Mass balance errors are reduced by using a Newton-Raphson iterative procedure. Root water uptake is described as follows:

$$S(h,z) = \alpha(h) * S_{\max}(z) \qquad (5)$$

where $\alpha(h)$ is a reduction function depending on the actual pressure head and S_{max} (d^{-1}) represents the maximum root water uptake at a certain depth. The root water uptake term is integrated from the soil surface to an increasing depth *z* less or equal to the rooting depth until the integral becomes equal to the potential transpiration rate. Otherwise water stress is considered to occur.

The soil moisture retention characteristic was described by the van Genuchten model :

$$\Theta(h) = \Theta_r + \frac{\Theta_s - \Theta_r}{\left[1 + (\alpha|h|)^n\right]^m} \qquad (6)$$

where θ is the volumetric water content (m^3 m^{-3}), *h* is the pressure head (cm), θ_r the residual water content (m^3 m^{-3}), θ_s the saturated water content (m^3 m^{-3}), and α

Table II. θ(h) and K(h) Parameters Derived from Pedotransfer Functions and Measurements (11 for the A_p-Horizon, 46 for the B_t-Horizon).

	θ(h)					K(h)		
Horizon *(m)*	$\theta_{sat}^{\dagger}$ $(m^3\,m^{-3})$	θ_{res} $(m^3\,m^{-3})$	α (cm^{-1})	n (-)	$m^{\ddagger}$ (-)	K_{sat} $(cm\,d^{-1})$	b (-)	N (-)
From pedotransfer functions:								
A_p: 0-0.4	0.40	0.11	0.0007	0.824	1.0	63.4	1.044	1.554
B_t: 0.4-1.1	0.38	0.15	0.0005	0.754	1.0	108.0	1.684	1.452
From measurements:								
A_p: 0-0.4	0.395	0.0	0.0016	1.5344	0.3483			
B_t: 0.4-1.1	0.438	0.0	0.0493	1.1174	0.1050			

†: calculated from bulk density, ‡: where m=1-1/n

Table III. Mean Values of Original and Transformed h(θ) Parameters.

Horizon	$\langle \theta_{sat} \rangle$	$\langle \ln \alpha \rangle$	*J(n)*
A_p	0.395	-6.34	2.04
B_t	0.438	-3.01	4.11

Table IV. Covariance Matrix of h(θ) Parameters for Two Soil Horizons.

A_p*-horizon*	*θsat*	*ln α*	*J(n)*
θ_{sat}	0.00019		
ln α	0.00174	0.16	
J(n)	0.00169	0.22	0.41
B_t*-horizon*	*θsat*	*ln α*	*J(n)*
θ_{sat}	0.00049		
ln α	0.00873	1.38	
J(n)	0.00165	0.6	0.38

(cm^{-1}), n (-), and m (-) are empirical parameters *(15)*. Hydraulic conductivity is calculated according to

$$K(h) = \frac{K_s}{1 + (b|h|)^N} \tag{7}$$

where K_s is the saturated hydraulic conductivity (cm d^{-1}), h is the pressure head (cm) and b (-), and N (-) are empirical parameter *(16)*.

Solute transport is described for the mobile soil region as follows

$$\frac{\partial(\Theta_m C_m)}{\partial t}+\frac{\partial(f.\rho.k_d.C_m)}{\partial t}=\frac{\partial}{\partial x}\left(\Theta_m.D_m\frac{\partial C_m}{\partial x}\right)-\frac{\partial(q_w.C_m)}{\partial x}+\alpha^*.(C_m-C_{im})-\gamma(\Theta,T,z)C_m \tag{8}$$

where θ_m is the mobile soil water content (m^3 m^{-3}), C_m is the solute concentration in the mobile soil region (kg m^{-3}), t is time, f is the fraction of adsorption sites situated in contact with the mobile region (-), ρ is the soil bulk density (kg m^{-3}), k_d is the linear solute distribution constant (m^3 kg^{-3}), x is the space co-ordinate (m), q_w is the Darcian water flux (m d^{-1}), α^* is an empirical transfer coefficient between mobile and immobile region, C_{im} is the solute concentration in the immobile soil region, γ is the source/sink term (d^{-1}), θ is the total soil water content (m^3 m^{-3}), and T is the soil temperature (°C). Accordingly, mass conservation in the immobile region yields

$$\frac{\partial(\Theta_{im}C_{im})}{\partial t}+(1-f).\rho.k_d\frac{\partial C_{im}}{\partial t}=-\alpha^*.(C_m-C_{im}). \tag{9}$$

Degradation of sorbed and dissolved solute has been allowed for following first-order kinetics. For the use in this paper subroutines were added to the model to correct degradation for the effect of soil moisture and soil temperature according to *(14)*

$$C_t=C_{t_0}*e^{\left(f*\left(\frac{\ln 2}{A*\Theta_g{}^{-B}}\right)*t\right)} \tag{10}$$

where C is the solute concentration (m^3 kg^{-3}), t is time, A and B are empirical parameters (-), θ_g the gravimetric soil moisture (kg m^{-3}), and f (-) a correction factor for the degradation rate coefficient as derived in the laboratory

$$f=Q^{\frac{(T-T_0)}{10}} \tag{11}$$

where Q is a constant (-), T_0 the temperature of the laboratory degradation study (°C).

Crop development can be specified by defining leaf area and root development as input or using the submodel SUCROS *(17)*. SUCROS calculates the crop development rate, dry matter accumulation rate and LAI (leaf area index) development rate depending on temperature and radiation conditions also considering the respective development stage. Potential evapotranspiration (ET_0, mm d^{-1}) is model input. Actual evapotranspiration is calculated by the model.

Simulation Strategy. To quantify the field scale behaviour monte-carlo simulations with the WAVE model were performed. In a first step (DT1L, DT1F) the WAVE model was tested and calibrated using the results from five lysimeter and hydraulic functions derived from pedotransfer functions according to *(12, 18)* (Table II). The calibration was done by comparing the mean observed and predicted soil moisture contents at different depths and subsequently changing parameters in order to achieve good agreement. A better description of the soil moisture profile was obtained by setting θ_{res} to zero in both layers, and changing the α parameter to 0.0035 and 0.0025 for the A_p and B_t soil horizon, respectively. In addition calibration of the crop growth module was essential to obtain better estimates of the actual evapotranspiration rates and calibration of root water uptake parameters in equation 5 was necessary. The potential evapotranspiration data and the crop parameters for winter wheat were also taken from Dust et al. (submitted for publication). In order to evaluate the effect of the artificial lysimeter boundary condition (L) a free drainage boundary condition (F) was imposed which better agrees with natural field conditions at Merzenhausen.

In total 6 different monte-carlo simulations were performed as shown in Table V. Also deterministic runs with the mean values of each parameter distribution were conducted for comparison. Each monte-carlo simulation consisted of 1000 runs with the WAVE model. For each run the parameters were drawn from specified univariate and multivariate normal distributions. Generation of a realization from these distributions was done using

$$\vec{Q} = L\vec{P} + \vec{u} \qquad (12)$$

where u is a vector containing the mean values, P a vector containing random numbers following a normal distribution with mean zero and variance 1. L is the lower triangular Choleski decomposition of the variance covariance matrix.

For each run, the 1.1 m soil profile was divided in 110 layers with 0.01 m thickness each. Initial water content for the simulations was set to the average volumetric moisture content obtained from the lysimeter data. For the numerical solution time steps were allowed to range between 0.26 and 0.01 d with the restriction of a maximum water balance error in one compartment of 0.01 $cm^3\ cm^{-3}\ d^{-1}$ and a maximum

Table V. WAVE Simulations with Two Bottom Boundary Conditions (Lysimeter / Free Drainage) Performed to Characterize Field Scale Behaviour.

	h(θ)	*K(θ)*	K_d	*Degradation*
DT1L DT1F	fitted	fixed	$<K_d>$	$<k>$
DT2L DT2F	$<h(\theta)>$	fixed	$<K_d>$	$<k>$
MC1L MC1F	variable	fixed	$<K_d>$	$<k>$
MC2L MC2F	variable	fixed	variable	$<k>$
MC3L MC3F	variable	fixed	variable	variable

$<h(\theta)>$: mean moisture retention characteristics parameters,
$<K_d>$: mean K_d-value
$<k>$: mean degradation rate constant,
L denotes lysimeter boundary condition, F denotes free drainage (flow under unit gradient)

change in water content of 0.012 $cm^3\ cm^{-3}$ per time step. The initial concentration of MBT in the soil profile was set equal to zero. To evaluate the effect of spatially variable K_d on MBT-profiles the median and P_5 and P_{95} percentiles of the centre of mass were calculated. The centre of mass for each individual simulation was calculated according to:

$$CM = \frac{\sum_{i=1}^{n} r_i d_i}{\sum_{i=1}^{n} r_i} \tag{13}$$

where i is the number of soil layers of the soil profile, r_i is the concentration of MBT in the i-th layer and d_i is the layer depth.

Results and Discussion

Soil Water Balance. Results of the experimentally determined soil water balance terms are shown in Table VI. On average the five lysimeters contained around 265 L of soil water at the start of the experiment (range: 246 L to 283 L). No runoff or ponding was observed in all lysimeters during the monitoring period of 252 days. Total precipitation was 473 L m^{-2} during this period. Leaching occurred during winter time in all lysimeters. Plant growth and warmer temperatures caused higher evapotranspiration in summer that did not allow for leaching. Considerable variation of the leachate volumes between five lysimeters was observed. An average amount of 104 L was collected in 252 days, the leachate volumes ranged from 72 to 140 L. An average decrease of soil water storage of -131 L (range -88 L to -162 L) was recorded after 252 days. Total actual evapotranspiration ranged from 421 L to 546 L (average 501 L).

The calculated drainage volume of 114 L and actual evapotranspiration flux of 444 L of run DT1L was within the range that was observed in the experiments (Table VI). The predicted change of soil water storage of -85 L was considerably lower than the observed mean and outside the experimentally observed range. Imposing a free drainage boundary condition (DT1F) resulted in considerably different soil water balance components. Total drainage volume increased to 163 L, as a result less water was stored in the profile. Actual evapotranspiration terms actually did not change substantially (Table VI).

Using the mean values of estimated $h(\theta)$ parameters, (DT2L) obtained from field samples, resulted in a drainage volume of 47 L which was lower than the observed mean value and outside the experimental range. As a consequence more water was stored in the soil profile in combination with increased actual evapotranspiration that was close to the experimentally observed mean value (Table VI). A similar behaviour was also found when using the free drainage boundary condition (DT2F). The lower drainage volume for DT2L and DT2F is explained by a higher θ_{sat} value of the B_t-horizon which results in a higher soil water storage capacity of the 0.4-1.1 m soil layer (Table II). The difference in drainage volume between the deterministic runs DT1L/F and DT2L/F is solely due to different moisture retention characteristics. In the DT1L/F runs the $h(\theta)$ parameters were estimated with pedotransfer functions and calibrated

Table VI: Results of Soil Water Balance Components of WAVE Simulations.

	Drainage (L)			*Change of soil water storage (L)*			*Actual evapotranspiration (L)*			*Runoff (L)*		
	$\bar{x}$	*range*		$\bar{x}$	*range*		$\bar{x}$	*range*		$\bar{x}$	*range*	
Experiment (n=5)	104	72 to 140		-131	-88 to -162		501	421 to 546		0	none	
DT1L		114			-85			444			0	
DT2L		47			-58			484			0	
DT1F		163			-126			436			0	
DT2F		78			-77			472			0	
	P_5	*Median*	P_{95}	P_5	*Median*	P_{95}	P_5	*Median*	P_{95}	P_5	*Median*	P_{95}
MC1L	3	51	115	-119	-56	25	407	481	509	0	0	10
MC1F	24	80	152	-148	-72	27	387	469	499	0	0	7

against soil moisture profiles of lysimeters. The *h(θ)* parameters for the runs DT2L/F were mean values obtained from modified multistep outflow experiments. This poses the fundamental question which method provides the most appropriate characterization of soil hydraulic functions

Considering field scale variability of the *h(θ)* parameters (MC1L, MC1F in Table V) resulted in distributions of predicted soil water balance components that were generally not normally distributed. These distributions are therefore better characterized by the median values and the P_5 and P_{95} percentiles rather than using the mean values and variance. In addition, it provides an easier way to compare distributions without requiring a transformation to normal distributions. Median values of water budget components were close to the results of the deterministic runs (Table VI). However, calculated variability of soil water balance components were larger than those observed in the lysimeter study for the drainage volumes and change in soil water storage for both boundary conditions (Table VI).

The calculated ranges of the soil water balance components for MC1L were larger than the experimentally measured variations (Table VI). It is not clear whether this is due to natural field scale variability of soil hydraulic properties, the effect of measurement errors or the limited number of lysimeters. The importance of measurement error was shown in an analysis of the multistep outflow data from the Merzenhausen field site where a large contribution of small scale variation was found which might be attributed to measurement errors *(11)*.

Total MBT Residues in Top Soil. MBT residues were sampled in one lysimeter after 252 days. In total 68.9 mg m^{-2}, corresponding to 27.8 % of the applied amount of the pesticide was determined in the top 0.1 m of the soil profile.

With the mean values of the degradation parameters (DT2L, DT2F) the WAVE model predicted 62.1 and 61.4 mg m^{-2} of residual MBT in the soil profile after 252 days. Thus the model underestimated MBT residues by about 10 % for both boundary conditions.

Runs MC1L and MC1F gave a median value of 60 mg m^{-2}. The respective ranges as expressed by the P_5 and P_{95} percentiles are equal to 55.5 - 67.0 and 55.7 - 67.4. Although variation of *h(θ)* parameters considerably affected soil water budget components it hardly influenced predicted total MBT residues in the soil profile as shown by the calculated ranges. This is independent of the type of boundary condition. This indicates that the effect of variation in soil moisture on total residues is not important for the prediction of field scale MBT residues. For values of b (equation 10) larger than 0.01 the impact on total pesticide residue predictions might be larger. This is also supported by results obtained with variable pesticide degradation parameters (MC3L, MC3F).

Using these variable degradation parameters derived from laboratory studies resulted in median values for total MBT residues in the soil profile of 94.7 and 93.1 mg m^{-2}, respectively. The corresponding P_5 and P_{95} percentiles were 3.9 -182.5 and 3.0 - 179.9, respectively. The large ranges are due to considerable variation in the estimates of the Walker parameters obtained from fitting residue data from laboratory degradation experiments to equation 10. This may be either due to spatial variability or measurement errors. The observed large scatter in residue data made it also difficult to verify the appropriateness of the applied first order kinetic approach.

Distribution of MBT Residues in Top Soil. In the deterministic runs DT2L and DT2F the centre of mass of MBT was at a depth of 9.4 and 7.7 cm below the soil surface after 252 days. This corresponds to a mean velocity of 0.037 and 0.030 cm d^{-1} which is only due to the effect of bottom boundary conditions. Results of the effect of a constant and variable K_d value on MBT residue profiles in combination with variable $h(\theta)$ parameters are presented in Table VII. The median of the centre of mass for the runs MC1L and MC1F was equal to 8.7 and 7.5 cm, respectively, giving a median transport velocity of 0.034 and 0.03 cm d^{-1}. Distributions of the centre of mass for both runs were non-Gaussian with a positive skewness of 1.4 and 1.7, respectively. This indicates that a majority of the calculated centre of masses were larger than 8.7 and 7.5 cm.

Using spatially variable K_d values in runs MC2L and MC2F resulted in identical distributions of the centre of mass as those obtained with the MC1 runs with constant K_d and variable $h(\theta)$ (Table VII). This shows that spatial variable K_d values are not important for the prediction of MBT residue profiles in soil. Variable soil hydraulic properties dominated the effect of spatially variable K_d as indicated by the P_5 and P_{95} values of runs MC2L and MC2F (Table VII). The effect of a larger median solute velocity of MBT for the lysimeter boundary conditions was also observed in runs with variable K_d and hydraulic properties.

MBT Residues in Leachate. During the 252 days monitoring period, traces of MBT were determined in the drainage, corresponding to about 0.01 and 0.05 % of the applied pesticide amount (Figure 1). In none of the simulations with the WAVE model, which uses the convection dispersion equation, MBT was predicted in the leachate. Also the use of the mobile/immobile soil water concept with a large range of θ_m/θ and α^* values did not simulate leaching of MBT. Calculating the effect of spatially variable K_d values and $h(\theta)$ parameters on the transport of MBT a median solute velocity of 0.03 cm d^{-1} for MC2L/F was obtained. The corresponding P_5 and P_{95} percentiles of the median solute velocity, as calculated from Table VI, were equal to 0.02 - 0.09 and 0.02 - 0.10 cm d^{-1}. These velocities are too small to explain the observed fast transport of MBT. This indicates that MBT in the experiments was most likely transported by means of preferential flowpaths or high hydraulic conductivity zones. In order to accu-

Table VII. Results of MBT residue profile simulations (centre of mass, cm) with the WAVE model.

	P_5	*Median*	P_{95}
MC1L	5.6	8.7	23.7
MC2L	5.6	8.2	23.7
MC1F	5.5	7.5	25.4
MC2F	5.5	7.5	25.8

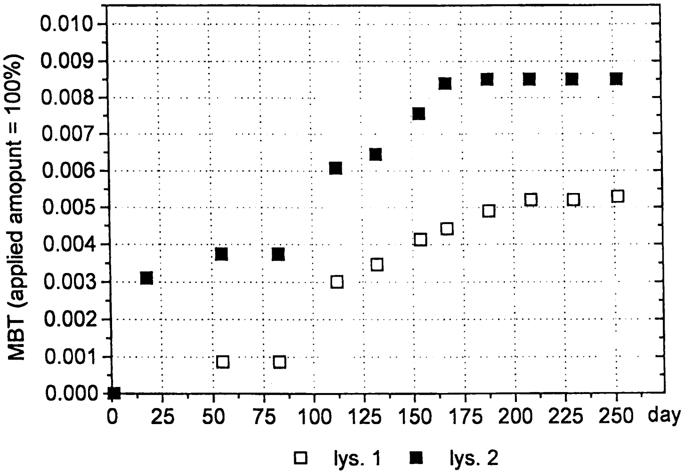

Figure 1. MBT-Residues in Leachates of Two Lysimeters Treated with MBT on November, 25 1988 During 252 Days.

rately predict pesticide transport in lysimeters, models should include a description of such transport mechanisms. Although conceptual approaches and models are available *(19)* preferential flow processes are not accounted for in many existing models used for risk assessment. A major obstacle for the use of preferential flow concepts remains their parameterization.

Conclusions

The present study showed that the estimated variation of leaching volume at field scale is considerably larger than the variation measured in five lysimeters. This number of replicates did not capture the impact of field scale variability on pesticide leaching in terms of drainage volume. The lower boundary condition of a lysimeter imposes a different hydraulic regime on the soil monolith, which results in different numbers of the soil water balance compared to the results obtained with a free drainage condition occurring at the field site. The free drainage boundary condition gave higher drainage fluxes as those obtained with a lysimeter boundary condition. For linear equilibrium sorption the spatial variability of the distribution coefficient is not relevant for predicting MBT soil residue profiles. Furthermore, variability of hydraulic properties was found to be more important for predicting transport of MBT than the effect of spatially variable sorption. Standardized degradation experiments showed a large variation in determining pesticide degradation parameters. Accounting for this variation in model simulations resulted in a huge variability of predicted pesticide residues. More research is needed to quantify the effect of natural variation of microbial decay processes on solute transport. Mathematical models should account for preferential flow mechanisms, if they are to be used to predict pesticide leaching.

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Chapter 15

An Industry Approach to the Application of the Lysimeter Concept

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Lysimeters are widely used tools for studying the environmental behavior of crop protection products. The principal advantages of such studies include the ability to use radiolabeled compounds, the confined nature of the studies permits good estimates of fluxes, and study conditions approximate those occurring in normal agricultural fields. Lysimeters can be valuable research tools to explore transport mechanisms in soil, aid in the development and validation of computer models (especially the hydrology portion), or to assess formation and mobility of metabolites of a potential product at an early stage in development. The lysimeter concept can also be extended to field studies; this is especially useful with spatially variable applications or to permit the application of radiolabeled compounds.

During the past two decades, lysimeters have become a widely used technique (especially in Europe) for studying the behavior of crop protection products in the environment (*1-3*). Lysimeter studies have been required for about 10 years for registration of potentially mobile compounds in Germany (*4*) and have also been included as an option in the more recently defined European registration process.

In this report the term lysimeter concept will be used to denote experimental studies conducted with intact soil cores to which crop protection products are applied and the leachate from the bottom of the cores is collected and analyzed. Large diameter lysimeters typically have a surface area of 0.5-1 m^2 enabling most crops to be grown under normal agricultural conditions. Small diameter lysimeters typically have a diameter of about 15 cm, too small to permit the planting of some crops.

The purpose of this paper is to illustrate how the lysimeter concept has been applied at Rhône-Poulenc (or in collaborative projects including Rhône-Poulenc) in the study of the environmental behavior of crop protection products. This includes a discussion of advantages and disadvantages of lysimeter studies compared to field and laboratory studies, a description of the large and small diameter lysimeter facilities at Rhône-Poulenc, examples of applications of lysimeter studies, interpretation of results, and modification of the lysimeter concept for application to field studies. The content of this paper is restricted to use at Rhône-Poulenc, but other papers have described the use of the lysimeter concept at DowElanco (*5-6*) and ECPA (*2*) provides a more general industry viewpoint.

Advantages and Disadvantages of Lysimeters

An understanding of the characteristics of lysimeter studies compared to laboratory and field studies is essential for the understanding of relative advantages and disadvantages. Important characteristics of these three types of studies are summarized in Table I.

Table I. Characteristics of Typical Laboratory, Lysimeter, and Field Studies

Study Characteristic	*Laboratory*	*Lysimeter*	*Field*
use of radiolabeled material possible	yes	yes	no
material balance obtained[1]	yes	yes	no
simulates actual field conditions	no	yes	yes
results dependent on climatic conditions	no	yes	yes
soil structure maintained	no	yes	yes
regular soil sampling throughout the study	yes	no	yes
ability to study behavior in subsoils	no	no	yes

[1] When volatilization losses are measured directly
SOURCE: Adapted from ref. *7*

One of the important advantages of laboratory and lysimeter studies is that the contained nature of these studies permits the use of radiolabeled compounds. This facilitates the analyses of the parent compound, allows for identification and quantification of metabolites, and permits determination of the amounts of bound residues. Since field studies usually cannot be conducted with radiolabeled material, the analytical methods used in these studies can only determine concentrations of parent and metabolites identified in previous laboratory studies. Because the use of radiolabeled compounds permits the quantification of parent, identified and unidentified metabolites, and bound residues in soil, leachate, and harvested foliage and crops, complete material balances can be obtained in laboratory studies. Although material balances are not complete in most lysimeter studies, since volatilization losses are usually assumed to be the difference between the amount of applied and the sum of the amounts found in soil, water, and crop samples, the use of radiolabeled compounds permits a more accurate determination of compounds found in each substrate. However, techniques for measuring volatilization losses in large-diameter lysimeters have been recently reported (*8*).

An advantage of lysimeters compared to laboratory studies is that degradation and movement are similar to field conditions. This is because soil temperatures, rainfall, evapotranspiration, and light intensity are usually nearly equivalent in lysimeter and field studies. A disadvantage of lysimeter studies compared to field studies is that degradation and movement cannot be studied in soils greater than about a meter below the soil surface. For some compounds, degradation in subsoils can be important in determining the magnitude of any residues reaching ground water. A disadvantage of both lysimeter and field studies is that study results are dependent on climatic conditions and irrigation practices. Therefore, results from studies conducted in different years can have very different results.

An advantage of both lysimeters and field studies is that soil structure is maintained, which is especially important when the mobility of a compound is being studied, but soil structure can also affect degradation rates. Transport mechanisms such as preferential flow through cracks, fissures, and earthworm burrows can occur in both lysimeter and field studies. However, preferential flow processes can result in quite different results in replicate lysimeters (as discussed later) so a field study might be more appropriate for determining concentrations in shallow ground water since the concentrations would be integrated over a larger area. Transport mechanisms occurring at a larger scale (such as runoff, drainage, and interflow) would be difficult to study in conventional lysimeters and are probably best studied in field experiments.

An advantage of lysimeter studies compared to field studies is the ability to quantify the movement of water below the depth of the lysimeter. In field studies water recharge can only be estimated indirectly by tracers or measurement of water content in soil samples. This is especially an advantage in checking the hydrology portion of computer models predicting the downward movement of crop protection chemicals in soils. A corresponding disadvantage of lysimeters is that soil samples cannot be collected deeper than 15-30 cm below the soil surface without affecting subsequent behavior. This means that collection of soil cores as a function of time to determine formation and decline of parent and metabolites as in a field dissipation study is not scientifically appropriate. Therefore, such information could only be obtained by destructive sampling with a significant increase in study cost. As a result of the lack of information on concentrations of parent and metabolites as a function of time and depth, typical large diameter lysimeter study results cannot be used effectively to validate the pesticide routines in computer models. However, the inability to determine behavior of parent and metabolites can be overcome in smaller diameter studies conducted with replicate lysimeters that can be removed and sampled at selected time intervals.

Large Diameter Lysimeters

Applications. The most common application of large diameter lysimeter studies by industry is to measure concentrations of crop protection products and metabolites in the leachate of a regulatory study conducted under specified conditions. Most regulatory studies conducted in Europe have followed the German guidelines (*4*) which require two replicate lysimeters containing a sandy soil with low organic matter, a surface area of 0.5-1 m^2, a depth of 1-1.3 m, at least 800 mm of rainfall and irrigation, and a study period of two to three years.

The objective of a European regulatory study is quite limited—Is the average concentration of parent and significant metabolites under 0.1 µg/L? In order to prevent any effect on mobility, soil sampling is limited to the end of the study. Therefore, little information is obtained on the degradation and transformation of parent and metabolites (except what can be deduced from the concentrations in the leachate). Even the leachate concentrations are not absolute results, since as mentioned earlier, these concentrations are a function of the specific weather conditions and irrigation procedures.

Often non-regulatory applications of the lysimeter concept, which are not confined to the rigid specifications of a regulatory study, result in greater contributions to the understanding of generic transport mechanisms or the behavior of a specific chemical. Since non-regulatory studies are usually designed to fulfill the specific objectives, such lysimeter studies follow no specific protocol. For example, two separate studies conducted in the U.K. (Brown et al., 1996, unpublished paper, and Bromilow, 1996, unpublished paper) have used lysimeters in two separate projects to better understand movement of crop protection products in cracking clay soils. In spite of the limitations discussed earlier, results of lysimeter studies have also been used in collaborative model validation projects. Two of these are a German project with the model PELMO and lysimeter studies submitted to German registration agencies (M. Klein, 1996, personal communication) and a Swedish effort involving blind predictions with various models of results for lysimeter studies conducted with several different soils (example papers from this effort include ref. *9-11*). As mentioned earlier, lysimeters have been used in Germany to study volatility (*8*). At Rhône-Poulenc, large diameter lysimeter studies have been conducted to better understand the behavior of new products.

Variability. In field studies, soil and soil-water samples are highly variable, with individual CV values for single soil samples in the order of 100 percent. As a result, 15-20 samples must be collected for each time and depth increment of a field dissipation study (*12*). Sources of this variability include soil structure, variations in soil properties, non-uniformity of irrigation and rainwater reaching the ground surface as a result of crop canopy and the method of irrigation, non-uniformity of transpiration losses, and variations in the initial distribution of a crop protection product. Conducting studies in confined systems such as lysimeters where the application amount is precisely controlled and soil layers and water samples can be homogenized prior to sub-sampling helps eliminate sampling variability due to non-uniformity of residues. However, the variability in movement of residues in apparently identical lysimeters remains. In studies with bromide and chloride with three different soils (*6*), breakthrough curves showed a great deal of variability between replicate lysimeters. In six tests conducted with sandy soils summarized in Table II (*13*), only relatively small differences in leachate volumes were observed between replicate lysimeters. However, radioactivity in lysimeter leachate varied by up to a factor of four between replicates. Variations in the levels of parent or significant metabolites found in the leachate was even greater, up to about a factor of twenty. There was no correlation between the variability observed in the lysimeter results and the properties of the various compounds. For example, test materials 2 and 5, showing the least and greatest variability, have very similar sorption and degradation properties.

Table II. Variability of Results between Replicate Lysimeters

Test Material[1]	*Leachate Volume*[2]	*Total Radioactivity in Leachate*[2]	*Parent or Significant Metabolite in Leachate*[2]
1	1.09	2.3	26
2	1.10	1.1	1.2
3	1.10	2.9	17
4	1.02	1.2	ND
5	1.02	4.0	>6.5*
6	1.00	1.3	ND

[1] The results are from the first year of studies conducted with six different compounds
[2] The variability is expressed as a ratio of the larger to the smaller
ND-not detected in leachate of either replicate
*detected in the leachate of only one replicate
SOURCE: Adapted from references *12* and *13*

In structured soil, interpreting lysimeter results can even be more difficult. For example, studies with lysimeters conducted on cracking clay soils showed that movement of water was much more rapid in soil monoliths collected over a mole drain compared to monoliths collected between mole drains due to cracks introduced during the moling process (A. Carter, 1993, personal communication).

The variability of results between replicate lysimeters is only considered superficially from a regulatory viewpoint. No guidance for interpreting results of a lysimeter study has been provided on an EU level. In Germany the replicate with the highest annual average concentration is used as the basis for deciding whether residues will exceed 0.1 µg/L. Ideally, evaluations of the results of lysimeter studies should consider both the variability between replicates as well as the year-to-year variability when applications are made during more than one year. Accounting for variability does complicate and introduce more subjectivity into the evaluation process. However, such evaluations have the potential of eliminating anomalous results and varying potentials for exceeding 0.1 µg/L due to differences in the specific rainfall pattern occurring during a lysimeter study.

Rhône-Poulenc Lysimeter Facility. In 1991 a large-diameter lysimeter facility was constructed at Aldams Farm near Manningtree, Essex, U.K. to conduct exploratory and registration studies with Rhône-Poulenc compounds. Although the lysimeter facility is similar to others in Europe, several novel features have been introduced which allow use of lysimeter cores readily available in the U.K., reduce cost, and reduce temperature effects. This lysimeter facility is described in detail elsewhere (*14*) so only the major differences from standard facilities are highlighted.

The heart of the lysimeter facility is 14 cylindrical soil cores 0.5 m^2 in surface area and 1-1.2 m in depth. Each core is enclosed in a GRP (glass reinforced plastic) cylinder and sealed into a galvanized pan. Advantages of GRP over stainless steel are reduced cost and thermal characteristics more similar to soil. These cores, essentially the same as used by many U.K. lysimeter facilities, are provided by the Soil Survey and Land Research Centre using the techniques described elsewhere (*5*).

The leachate collection system is significantly different from the common procedure of collecting leachate in a sump at the bottom of each lysimeter, which is then pumped out at specified intervals. As illustrated in Figure 1, leachate is transported from the bottom of the lysimeter via stainless steel tubing to collection vessels housed 4-8 m away in a 2 m deep concrete lined pit with a covering shed. The simplicity of this design reduces cost and helps avoid cross-contamination between lysimeters since no pumps or associated sampling equipment is required. The use of a simple collection pit also avoids the expense associated with underground chambers used at some facilities. Because the lysimeters are located away from the collection pits, good simulation of normal field temperatures and other conditions is ensured.

Each lysimeter is surrounded by a 2 m square netted cropped area. Individual nets (for exclusion of birds and animals) have the advantage of easy removal and are cheaper than a wire mesh covering the entire facility.

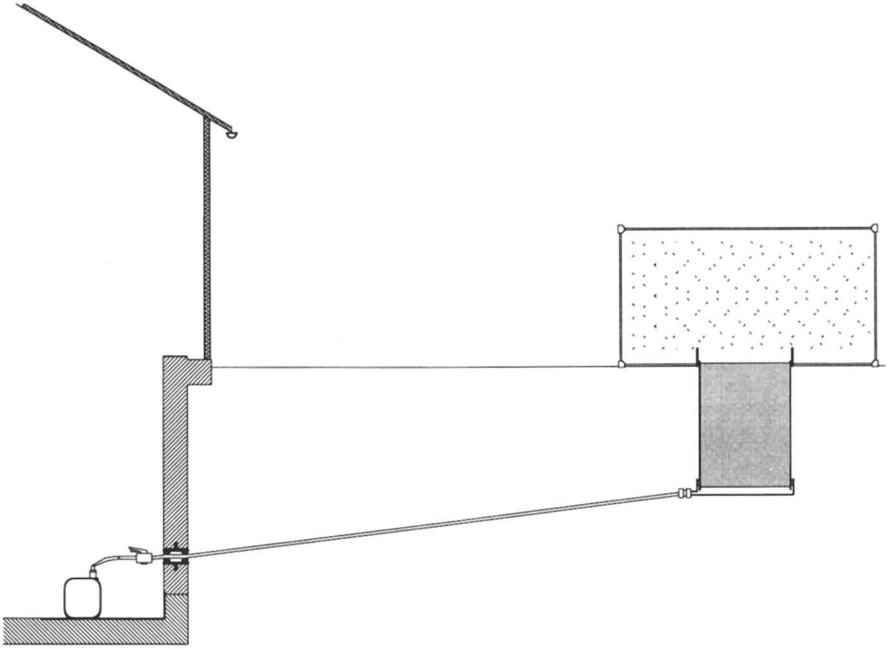

Figure 1. Leachate Collection at the Manningtree Lysimeter Facility

Small Diameter Lysimeters

Applications. The relatively small size of these lysimeters (typically about 15 cm in diameter) greatly reduces the effort (and associated cost) required to collect, install, and sample these lysimeters compared to standard large diameter lysimeters. Facilities for handling smaller diameter lysimeters can also be relatively inexpensive Therefore, conducting studies involving relatively large numbers of lysimeters becomes feasible if small diameter lysimeter studies are used. Small diameter lysimeters have at least two major disadvantages compared to large diameter lysimeters. Growing a crop (except for small crops such as turf or cereals) is usually not feasible. Edge effects, which can influence residue movement under certain conditions, will be greater in small diameter lysimeters.

During the last few years at Rhône-Poulenc, small-diameter lysimeter studies have been increasingly used to provide an early estimate of behavior of potential new products under field conditions (*15*). In these studies, radiolabeled compound is applied to the surface of 6-12 tubes containing undisturbed soil cores (0.15 m diameter by 1 m long). At appropriate intervals after application, tubes are removed from the experiment and divided into segments by depth. These samples are analyzed to determine the quantity and composition of the radiolabeled material remaining. Leachate from the cores is also collected periodically and analyzed.` These small-diameter lysimeter studies are relatively inexpensive and can be started as soon as radiolabeled material is available (prior to or concurrent with the conduct of most laboratory studies). Therefore, information on the principal metabolites formed under field conditions and the persistence of parent and metabolites can be obtained well before cold (non-radioactive) soil methods for parent and metabolites are available to permit conducting normal field trials.

Small Diameter Lysimeter Facilities. A number of designs have been used for such facilities (one example similar to that used at Rhône-Poulenc is described in ref. *16*). At Rhône-Poulenc up to 12 small diameter lysimeters are placed outdoors in a fiberglass box (1 x 1 x 1 m) supported by metal legs (*15*). These lysimeters consist of soil cores taken by pushing a PVC pipe (the bottom edge is chamfered on the outside to reduce resistance) into the soil. After the lysimeters are inserted into the box, the remaining volume is filled with sand to more closely simulate soil temperatures under field conditions. Glass wool and stainless steel mesh are placed at the bottom of the core. A stainless steel funnel sealed to the bottom of the PVC tube directs leachate into a brown glass bottle. During the conduct of the study, water may be added to the surface of the lysimeters to supplement that received due to rainfall. Soil cores are sampled by using a small angle grinder mounted in a timber rig to longitudinally cut open the PVC tubes, after which the core is divided into appropriate increments and placed into appropriate sample containers.

Field Studies

At Rhône-Poulenc the lysimeter concept has been extended to field studies by placing a number of tubes like those used in the small diameter lysimeter studies in a field plot. Each tube is driven into the ground with the bottom left open providing an undisturbed connection with deeper soils. Application of a specific amount of the product being tested is made to each tube usually at the same time as the crop is planted. Tubes are removed from the plot at desired intervals and sampled in a manner similar to that previously described for small diameter lysimeters.

Advantages/Disadvantages. The main advantage of this approach is that a known amount of material is applied to each tube and that these residues are confined to a specific volume of soil during the study. Therefore, as with lysimeters, all of the soil from a layer can be homogenized during sampling, eliminating variability due to spatial non-uniformity of residues. Because the application is confined, the use of radiolabeled compounds is also possible, allowing identification and quantification of metabolites and bound residues.

Disadvantages of this approach include that it is not suitable for simulating transport mechanisms occurring at a larger scale, such as drainage and interflow. The approach is also not suitable for situations where the crop protection product can move below the tube. The approach is also not suitable for relatively large crops, although using larger diameter tubes (for example 30 cm) makes such studies possible for crops such as potatoes.

Applications. Conducting studies inside lysimeter tubes has been used at Rhône-Poulenc for meeting soil dissipation requirements in two different circumstances. One is to permit use of radiolabeled compounds when an objective was to identify and quantify metabolites of a compound which formed numerous metabolites during the degradation process. The other circumstance has been to measure dissipation rates (using either radiolabeled or non-radiolabeled compounds) when the spatial non-uniform application (for example, from a seed treatment) has made it difficult to obtain representative samples in a traditional field study. (Although the normal way to obtain soil dissipation information on a seed treatment is to collect soil samples following a spatially uniform soil-incorporated application, sometimes the proximity of the compound next to the seed results in increased degradation. In such cases, studies using lysimeter tubes can be used to obtain degradation rates under actual use conditions.)

Conclusions

The lysimeter concept is an important tool in studying the environmental fate of crop protection products. Major advantages of this approach include the ability to use radiolabeled compounds, study conditions approximate those occurring in agricultural fields, and the confined nature permits an accurate determination of fluxes. Large diameter lysimeters are a useful tool in exploratory studies to better understand transport mechanisms such as macropore flow and volatilization. Considerable variability in leachate concentrations can occur between essentially identical replicates, presumably due to differences in soil structure, or from year to year in an individual core due to differences in climatic conditions. Currently this variability is only considered superficially from a regulatory viewpoint. Small diameter lysimeter studies are helpful for evaluating the environmental behavior of potential crop protection products and their metabolites at an early stage in development. Extending the lysimeter concept to field studies can be useful, especially when in studies where applications are not spatially uniform or when it is necessary to characterize numerous metabolites or bound residues.

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Chapter 16

Evaluating Pesticide Fate and Transport: I. The Use of Lysimeter, Field, and Groundwater Monitoring Studies

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Monolith lysimeters are not required for pesticide registration nor are they used routinely for evaluating the fate and transport of pesticides in the United States. Lysimeters may serve as a valuable link in the interpretation of laboratory and field environmental fate data for pesticides. However, several factors need to be considered in this interpretation, including 1) spatial variability of soil and site properties; 2) soil hydrology; and 3) tracking of the pesticide. Lysimeter design can cause unpredictable experimental artifacts in soil hydrology which may not represent actual field conditions. Natural water flow pathways in the soil may be disrupted through barrier effects of the lysimeter wall and disruption of the hydraulic gradient at the lower boundary of the lysimeter. Analysis of in-situ soil morphological and physicochemical properties provides important information for interpretation of lysimeter data. The link between field and lysimeter data can be evaluated using spatial variability information of soil properties and mass balance analysis. Spatial variability data can aid in designing the lysimeter at a scale appropriate to better represent natural field conditions.

In the United States, the U.S. Environmental Protection Agency (USEPA) relies on a combination of laboratory and field tests to assess the fate and transport of pesticides in the environment. Laboratory studies carried out under controlled conditions evaluate individual degradation pathways and identify and characterize transformation products. Hydrolysis and photolysis studies evaluate chemical degradation; metabolism studies

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[1] The views expressed are those of the authors and do not represent the views or policy of the U.S. Environmental Protection Agency.

In The Lysimeter Concept; Führ, F., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 1998.

evaluate biotic degradation. Mobility studies (batch equilibrium and soil column leaching) evaluate the likelihood of a pesticide to move through the soil. Properly-designed field dissipation studies can assess the combined mobility, degradation, and dissipation of pesticides and transformation products under actual use conditions.

When persistence and mobility data for a pesticide suggest a potential to contaminate ground water, USEPA requires field-scale (0.8 to 2.0 ha) ground-water monitoring studies as the final tier in the assessment of this potential. This study directly determines whether pesticide residues reach ground water. Typically one or two studies are conducted, although as many as eight studies have been required, depending upon the pesticide use area.

Results of field studies designed to evaluate the leaching potential of a pesticide will be difficult to interpret without an experimental design that addresses variability in the field and a good understanding of how a pesticide behaves under the range of field conditions. Site variability includes heterogeneity in soil properties with depth, poorly-quantified hydrologic factors such as preferential flow, and spatial variability in soil properties across a field. Other factors affecting pesticide fate in the field include climate (precipitation, temperature, wind), surface condition (bare-ground or cropped), runoff, and spray drift.

Field-scale dissipation and ground-water monitoring studies represent typical use conditions under natural settings with sites and agronomic practices that are likely to favor leaching. Because the sites are contiguous with the natural environment, landscape, and hydrology, field-study results integrate all factors affecting pesticide fate and transport. As with all field studies, field-scale variability may affect study design and interpretation. Environmental conditions in field studies are not controlled (*1, 2*).

Many European countries use lysimeter studies, rather than field or ground-water monitoring studies, as the final tier of their regulatory process for assessing the ground-water contamination potential of a pesticide. Monolith lysimeter studies provide a closed soil system which allows for greater control over environmental conditions and the capacity to use radiolabeled pesticides. The use of radiolabeled chemicals facilitates mass balance determinations and tracking of residues among various environmental compartments (soil, plant, leachate, air). The scale of observation afforded by the lysimeter may not be representative of sample or site conditions and may not adequately represent soil and site variability. The monolith lysimeter is isolated from the surrounding landscape, eliminating interactions such as surface runoff, lateral subsurface flow, continuity of pores and hydraulic potential gradient at the bottom of the lysimeter, and seasonal water table fluctuations. As a physical model, the lysimeter focuses on certain transport processes (leaching) over others (surface runoff, lateral flow). The lysimeter walls may interact with water flow, root growth, and soil swelling/shrinking to create artificial transport conditions (*1-7*).

Lysimeter studies can link laboratory and field studies to further assess routes of pesticide dissipation under field-like conditions (*1, 4*). Three factors in particular need to be considered in comparing and interpreting results from monolith lysimeter and field/ ground-water monitoring studies:

(1) Soil and field spatial variability
(2) Soil hydrology interactions with the study design
(3) Tracking the pesticide through various environmental compartments

This chapter assesses the potential impact of the first two factors on interpretation of monolith lysimeter results and makes recommendations for improving the study designs. The next chapter considers mass balance and pesticide tracking for ground-water monitoring and lysimeter studies.

Soil and Field Spatial Variability

The spatial variability of measurable soil properties such as infiltration rate, hydraulic conductivity, organic matter and clay contents, cation exchange capacity, density, frequency and distribution of large continuous pores (macropores), and microbial biomass are well-documented (*8, 9*). These factors influence the fate and transport of pesticides in the environment. Inadequate consideration of spatial variability in field experimental design results in increased uncertainty in results, inadequate characterization of the range of preferential flow pathways, and difficulty in extrapolating results to other sites, conditions, or soils.

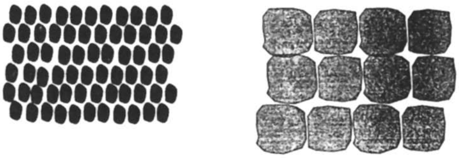
Appropriately-designed leaching studies should consider macroporosity and preferential flow paths, vertical heterogeneity from soil horizonation, spatial variability of soil and site properties on a variety of scales, and hydrologic impacts on pesticide movement. Ground-water monitoring studies are often conducted on sites with relatively homogeneous soils to minimize sampling and simplify data analysis. Lysimeter studies often select sites which are not prone to preferential flow (*4*). However, results of studies on relatively homogeneous soils with few macropores may be of little use in understanding pesticide leaching in soils with significant preferential flow paths (*10*).

Soil surveys describe variability in soil properties on a landscape scale and can serve as a useful tool in designing pesticide leaching studies (*10-12*). Incorporating variability of soil properties into environmental fate assessments may provide important information on the scale dependence and uncertainty of processes affecting pesticide fate and transport through the vadose zone.

Individual Sample Variability. Variations in leaching at the sample scale reflect local soil variability in organic matter, texture, structure, density, and porosity. Attempts to characterize soils on the basis of one property, such as texture, rarely provide sufficient information to predict the extent of pesticide leaching in soil. Textural class designations, such as sandy loam, loam, or clay, reflect the distribution of the individual particle sizes in a soil. However, a silt loam in Florida is not going to be the same as a silt loam in Germany because of the interaction of the other soil properties.

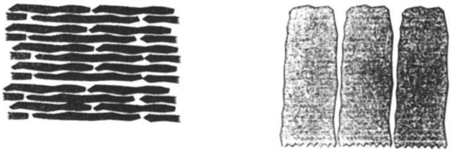
Individual soil particles are often aggregated into larger structural units, called peds, which affect pore distribution and resulting water flow and transport. The ped is a natural unit of soil structure which may take on different forms and sizes (Figure 1). The structural arrangement present in the soil affects the arrangement of soil pores, which will influence solute adsorption within and transport through the soil. Lysimeters maintain soil aggregation and thus approximate "natural" soil conditions.

Soil porosity includes small pores between individual particles (often <30-50 μm in diameter), planar pores between the natural structural units, and cylindrical pores formed from plant roots and burrowing animals. Networks of large (from 30-50 μm to



(A) Granular
spherical
<1 to >10 mm in
diameter
surface horizons

(B) Blocky
blocklike; rounded to
subrounded edges
<5 to >50 mm in size
subsurface horizons



(C) Platy
flat, width > length
<1 to >10 mm thick
subsurface, compacted
horizons

(D) Prismatic
columns; length > width
<10 to >100 mm wide
subsurface horizons

Figure 1. Structural units (peds) commonly found in soils.

>5000 μm in diameter), continuous or interconnecting planar and cylindrical pores (macropores) can serve as primary conduits for water and solutes through the vadose zone to ground water (*13-16*).

In order to capture the variability in soil hydrologic properties and solute transport likely to occur from the variability in soil properties, Bouma (*10, 11*) recommends a minimum representative sample volume of 20 to 30 peds. The size of peds typically varies with the type (shape and arrangement) of the ped (Figure 1). Two soils from central Pennsylvania (*17*) illustrate how differences in representative sample volume affect soil hydrologic properties and, thus, ideal lysimeter size.

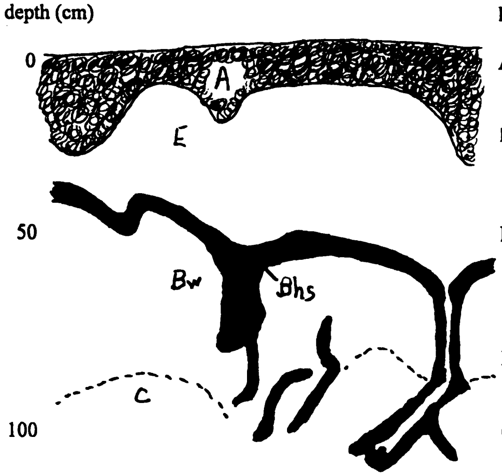
The Gatesburg (Leetonia Variant) soil, a Spodosol (*coarse-loamy, siliceous, mesic Entic Haplorthods*), is a loose sandy soil (>80% sand) with little or no ped formation (*17*). The irregular, undulating nature of the soil horizons (Figure 2) reflects variations in water flow and transport of soil constituents. A minimum sample area of 0.5 m x 0.5 m is needed to capture the 10- to 20-cm wide horizon boundary undulations common to this soil.

Hagerstown, an Alfisol (*fine, mixed, mesic Typic Hapludalfs*), is a clayey soil (maximum clay concentrations range from 50 to >70%) dominated by blocky peds, approximately 2 to 5 cm in diameter (Figure 3) (*17*). Water and solute transport through this soil often includes substantial preferential flow along the pores between the peds and through cylindrical biopores. A minimum sample area of 0.25 m x 0.25 m may be adequate to include variability from the blocky structure; a much larger area may be needed to include the network of continuous macropores.

Field Scale Variability. Soil surveys capture major landscape variations by separating soils into mapping units. Most detailed soil surveys in the United States are conducted at a scale between 1:12,000 and 1:24,000, with a minimum mapping unit delineation size of 0.6 to 2.3 ha (*18*). At best, up to 25% of these mapping unit delineations may contain inclusions of dissimilar soils (*18*). Field studies may encompass more than one mapping unit. Even in apparently "uniform" fields, variation in soil properties will occur. For this reason, multiple samples are necessary to characterize soils in the field before a sampling strategy for leaching studies is designed. An awareness of the spatial pattern of variability is important for selecting sites for leaching studies so that meaningful interpretations can be obtained from these studies.

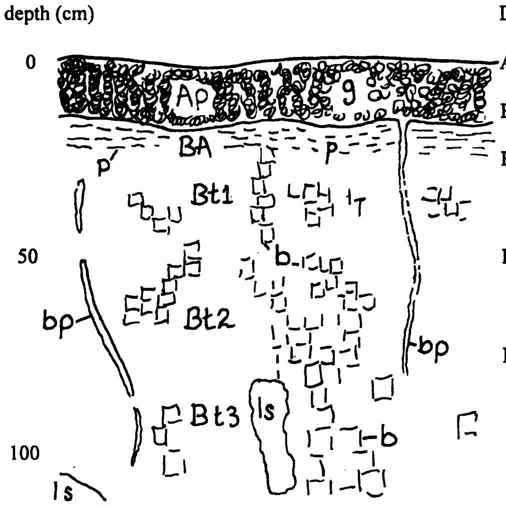
Jabbro et al (*19*) measured the in-situ saturated hydraulic conductivity (K_{sat}) in selected central Pennsylvania soils at 1-m intervals along a 40-m transect at a depth of 0.5-0.6 m with a constant-head, bore-hole permeameter. Hydraulic conductivity, the proportionality factor in Darcy's law equivalent to the flux of water per unit gradient of hydraulic potential (*20*), is a measure of the ease or difficulty with which water flows through soil. This study included the Gatesburg and Hagerstown soils illustrated in Figures 2 and 3.

The Gatesburg soil had the greatest range in K_{sat} values (Table I) and showed a significant spatial trend up to 4 meters (*19*). While most of the sample points had K_{sat} values <0.5 m/day, several points had measured values >2 m/day. The spatial variation reflected the undulating pattern seen in the soil profile. The maximum K_{sat} values in both soils probably represent areas of preferential flow, which are not uncommon even in sandy-textured soils (*14*). K_{sat} values in the Hagerstown soil (Table I) followed a



	Description
A	dark brown, loose, loamy sand
E	very pale brown to light gray, loose, sand to loamy sand
Bhs	dark reddish brown, friable, loamy sand; irregular boundary follows old root channels (now filled)
Bw	reddish yellow, friable, loamy sand to sandy loam
C	reddish yellow to yellow, friable, loamy sand to sandy loam

Figure 2. Drawing of a typical Gatesburg soil profile (based on a photograph by the author).



	Description
Ap	dark brown silt loam; granular (g) structure
BA	loam; weak platy (p) structure
Bt1	yellowish red silty clay loam; moderate blocky (b) structure; few biopores (bp) [root channels, earthworm holes]
Bt2	yellowish red silty clay to clay; strong blocky (b) structure; few biopores (bp)
Bt3	yellowish red to red silty clay to clay; moderate coarse blocky (b) structure; limestone (ls) fragments

Figure 3. Drawing of a typical Hagerstown soil profile (based on a photograph by the author).

curvilinear cycle of greater than 40 meters, influenced by changes in texture, structure, and variable depth to bedrock (*19*). Preferential flow pathways are more sparsely distributed in the Gatesburg soil. The high standard deviation and a much lower median than mean K_{sat} value suggest that preferential flow paths have a potentially greater impact on leaching assessments in the Gatesburg soil than in the Hagerstown soil.

Table I. Saturated Hydraulic Conductivity Values For Two Pennsylvania Soils Along a 40-m Transect

Soil	*Saturated Hydraulic Conductivity (meters/day)* *Range*	*Median*	*Mean*	*S.D.*
	Measured Values			
Gatesburg	0.03-2.40	0.16	0.53	0.70
Hagerstown	0.01-0.34	0.11	0.12	0.08
	Simulated Values (Summary of 10 Sets of Simulations)			
Gatesburg	0.03-7.58	0.15	0.50	0.71
Hagerstown	0.001-0.71	0.11	0.12	0.09

SOURCE: Measured values based on ref. 19.

While such extensive sampling along transects is often not feasible for field studies, stochastic model simulations using multiple results can help quantify uncertainties associated with variations in soil properties and pesticide leaching (*21*). A GEOSLIB (*22*) model used semivariograms generated from the field data to simulate K_{sat} values in a similar 40-m transect. The simulated median and mean K_{sat} values were similar to those measured in the Pennsylvania study (Table I). The simulated ranges for both soils were greater than those measured in the field.

Hydraulic conductivity is not the only factor affecting pesticide transport through the vadose zone. However, the range of K_{sat} values found in these soils illustrates the degree of variability that can exist. One lysimeter will not represent the range of field conditions in any of these soils. A site selected at a peak, or maximum, K_{sat} value may provide a high-end estimate of leaching within that soil while a site with a low K_{sat} value may underestimate the overall potential for leaching in that same soil type.

Regional / National Variability. Sites where field and ground-water monitoring studies are conducted or where lysimeter monoliths are taken need to be representative of the appropriate pesticide use pattern. A use pattern that has a wide geographic extent or a pesticide with multiple crop uses will likely cover a variety soil and hydrologic conditions. For this reason, several study sites are often necessary to characterize the range of anticipated behavior of a pesticide in the environment. In the United States, the U.S. Department of Agriculture's Natural Resource Conservation Service has established benchmark soils in each state and land resource region. Benchmark soils are geographically-extensive, agriculturally-significant soils that are usually well-characterized. By selecting benchmark soil series and hydrogeologic sites representative of pesticide use areas, field study results can be linked to known soil and hydrologic properties for broader extrapolation of results and for comparative risk assessments.

Hydrologic Considerations In the Lysimeter Study Design

Although the lysimeter study preserves soil horizonation and structure in a controlled environment for testing, it may not be representative of soil hydrology under field conditions. This is because inherent variability in soil properties, artificial boundaries, and initial conditions within the lysimeter may not adequately reflect real world conditions. The upper boundary is controlled by internal (soil and plants) and external (precipitation and evaporation) factors, whereas, the bottom conditions, if infinite in depth, are controlled by soil properties. Vertical boundaries will be influenced by internal and external factors and position (run-on, run-off, lateral flow, plant roots). Thus, factors which influence boundary conditions, such as water flow physics at the top or bottom of lysimeter, disruption of the hydraulic continuum and lack of run-off/run-on and lateral flow, and edge/wall and confined volume effects on macropore flow, soil shrink-swell, and plant root growth, will influence pesticide movement within a lysimeter.

The rate at which water enters the lysimeter at the surface will depend upon the rate of water input, soil infiltration rate or capacity, and initial soil water content, and will not include run-off or run-on water. When the soil surface is permeable, the water content is less than saturation, and water is applied at rates less than the infiltration rate, water will enter the soil, flowing through the soil matrix in response to the soil matric potential. When water input at the surface exceeds the infiltration rate or capacity, excess water flows into macropores. This preferential, or by-pass, flow is a natural process in which free water and solutes move through the soil along preferred paths (such as macropores) through the soil. Weber and Keller (*23*) observed macropore-influenced flow in soil column field lysimeters in a Plinthic Kandiudult soil in the coastal plain of North Carolina. Tritium, used to track the water front through the lysimeter column, moved down macropores first, then through the soil matrix, resulting in an "icicle-like" distribution at each soil depth. The greatest variability in flow was likely due to plinthite nodules and zones which diverted water movement somewhat; no wall-flow or core-flow was apparent (*23*). Preferential flow may "short-circuit" solute transport along the wetting front (*13*).

Within the soil profile, water will enter macropores when the water content reaches saturation and water pressure in the soil matrix is greater than the atmospheric pressure in the macropore. A pressure differential may exist at the bottom of the lysimeter between the soil and the leachate collection device which may interfere with soil water flow. Water will flow out of the soil in the lysimeter only when a sufficient water accumulation, usually near saturation, occurs to overcome this pressure differential (*20*). In field soils, water may move upward from deeper, wetter soil horizons into the overlying, drier soil. In a lysimeter monolith, upward flow from evapotranspiration may occur but the reservoir from underlying wetter horizons is disrupted. The presence of a leachate collector at the bottom of a 90-cm long soil column field lysimeter reduced the mobility of a mobile pesticide (metolachlor), with 4% more pesticide remaining in the upper 4 cm and 4% less in the 11- to 88-cm section compared to similar lysimeters which remained in contact with the underlying soil (*23*). The difference in mobility was attributed to reduction in downward movement of the pesticide or in interruption of upward movement in capillary flow at the bottom of the lysimeter. Weber and Keller (*23*) noted that drops hung from the bottom of the soil column equipped with a leachate collector until they grew sufficiently large to fall into the collector.

The complex nature of pesticide transport under macropore conditions depends on the rate and distribution of water applied to the lysimeter, pesticide application (surface-applied or incorporated), pore distribution and geometry, presence of natural or artificial restrictive layers, and the organic matter content and distribution. In structured soils, partial displacement of soil water occurs when much of the rainfall or irrigation water flows in macropores (*24*). In unsaturated soil conditions, water flow remains within the soil matrix, entering macropores only when the water pressure in the soil matrix is greater than the atmospheric pressure in the macropore. Layered soils with highly contrasting soil textures (clayey soil materials over sandy soils) may also hinder water flow, allowing water contents to increase so that water can flow from the clayey soil into the sandy soil.

The tendency of soils to expand (swell) on wetting and shrink on drying depends upon the amount and mineralogy of the clay, soil structure, and organic matter content. In clayey and silty soils, volume changes of 5% or more may occur (*25*). Swelling tends to reduce or close macropores while shrinking opens cracks in the soil. In natural conditions, swelling closes small cracks at the soil surface and reduces infiltration over time (*20*). Soil swelling and shrinking may interact with the lysimeter wall, closing off macropore flow during wet conditions and opening channels along the wall during dry conditions.

Roots and soil organisms open up potential preferential flow pathways. The type and extent of interactions depend on the health and rooting behavior of plant, irrigation/ rainfall scheme (amount and distribution), length of time for growth, and size of lysimeter. Growing plants (soybean and bermuda grass) greatly reduced and wheat straw mulch increased the mobility of a mobile pesticide (metolachlor) in a soil column lysimeter compared to a fallow lysimeter (*23*). The difference was attributed to more water uptake by plants and less soil moisture -- columns with plants had 68% less leachate and 34% lower soil moisture levels than columns without plants (*23*).

The lysimeter wall serves as a barrier to free root growth. Because of local differences in moisture along the wall, root growth may proliferate, providing preferential flow pathways for water and pesticide transport. Lysimeter walls can act as confining boundary conditions by isolating the soil profile from the surrounding landscape and hydrologic continuum, resulting in exclusion of surface and subsurface lateral flow, separation from underlying continuous pores and saturated zones, different patterns of water and solute redistribution from evapotranspiration and capillary action, and different water contents and distributions, often less than the surrounding soil (*26*).

An understanding of the distribution of macropores in the soil is critical to designing and interpreting lysimeter studies. Sample bias may occur when continuous macropores dominate flow paths in a small lysimeter or when the area of a small lysimeter excludes these pathways (see earlier discussion of representative sample sizes to encompass preferential flow paths). The inclusion of a conservative tracer, such as bromide, applied in the same manner as the pesticide, may aid interpretation of hydrologic interactions within the lysimeter.

Conclusion

Monolith lysimeter studies serve as a valuable link in interpreting laboratory and field environmental fate data for pesticides. However, design, interpretation, and comparisons of lysimeter and field data need to consider spatial variability of soil properties and soil hydrology.

An understanding of spatial variability in soil properties is important in assessing the field representation of both lysimeter and field study data. Marked variability of soil properties, particularly saturated hydrologic conductivity (K_{sat}), is commonly observed in field soils. Representative sample sizes that incorporate local variability depend on soil properties and should be based on soil characteristics. Natural field scale variability can be described using variograms derived from standard geostatistical analysis and stochastic model simulations (21, *27*). Alternatively, the variability of soils at different scales can be derived from soil surveys and GIS data analysis. An analysis of spatially dependent soil data can provide an estimate of the number of lysimeters and the representative sample volume needed to address soil variability. Locating field or lysimeter study sites on benchmark soil series and hydrogeologic sites representative of pesticide use areas facilitates broader extrapolation of the results and comparative risk assessments.

The lysimeter design imposes limitations on water movement because of disruption or alteration of "natural" water flow. The most obvious problem is the impact of the lysimeter wall on both preferential and lateral flow. The effects on preferential flow are likely to be accentuated in highly structured soils. Additionally, the lysimeter wall will impose a physical barrier to both subsurface lateral and overland flow pesticide transport processes. The lysimeter will serve as a barrier to root growth, resulting in root proliferation along the soil-wall interface. Such conditions may enhance evapotranspiration of plants and hence dramatically reduce water flow through the lysimeter.

The lower boundary condition of a lysimeter may influence the transport of water and solutes. The hydraulic gradient is disrupted at the lower lysimeter boundary. This disruption affects the downward flow of leachate through the soil column and cuts the lysimeter off from underlying continuous pores. Leachate moving through the lysimeter monolith will "hang" at the boundary until the pressure differential between the soil pores and the void is overcome. This occurs when the soil nears saturation. In addition, the disruption severs the hydrologic connection with shallow ground waters, isolating the soil in the lysimeter from fluctuating water tables and capillary rise during evapotranspiration. As a result, the soil moisture content in the lysimeter is likely to be lower than in the surrounding undisturbed soil.

Evaluation of monolith lysimeter study data must consider the question of whether by-pass flow is a natural process or simply an artifact in lysimeter design. Interpretation of lysimeter results should consider the interactive effects of soil properties, environmental conditions, and water flow conditions on solute movement.

Based on our scientific assessment, lysimeters can serve as a valuable link between laboratory and field studies. The major advantage of lysimeters is the ability to quantitatively track pesticide residues. These data, however, need to be considered in light of the soil properties.

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Chapter 17

Evaluating Pesticide Fate and Transport: II. Mass Balance and Tracking

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The U.S. Environmental Protection Agency (USEPA) has relied on the small-scale prospective ground-water monitoring (SSGWM) study to evaluate the ground-water contamination potential of mobile and persistent pesticides for a number of years. Unlike in monolith lysimeter studies, mass balance of the applied pesticide cannot be determined in open field studies (such as the SSGWM study) without making assumptions about the distribution of residues in the subsurface environment. However, the recommended vadose zone pore-water and saturated zone ground-water sampling scheme in SSGWM studies may facilitate an approximation of mass balance of many pesticides with high leaching potential for an extended period. In one example, the mass of pesticide residues (including degradates) in ground water and the lower part of the vadose zone nearly two years after application represented the majority of the originally applied material. This high mass balance in a field study can be attributed to a combination of adequate sampling design and a high environmental persistence of pesticide residues. Open field studies like the SSGWM study and closed-system studies like the monolith lysimeter studies can be used together to provide a more complete picture of how leaching amounts relate to the level of ground-water contamination that may occur and how much mass of the pesticide is likely to leach under a variety of conditions.

In the United States, regulations on pesticide use are designed to prevent ground-water pollution and to protect human health. The most recent legislation requiring regulation of the ground-water and surface-water impact of pesticide use is the Food Quality Protection Act of 1996. This Act requires that the Agency specifically determine concentrations of pesticides that may occur in drinking water as a part of dietary exposure assessments (*1*); the Agency must take action to ensure that pesticide dietary exposure will not occur at toxicologically significant levels. When a pesticide is determined to be a potential ground-water (or surface water) contaminant, USEPA must set health-based limits on residues in drinking water (regulatory limits are called Maximum Contaminant Levels, or MCLs) for that pesticide (*2*). These standards are based on the no-effect and low-effect levels determined in toxicity tests with mammals and therefore an MCL for a given pesticide could be much higher than 0.1 $\mu g\ l^{-1}$, the European Community standard for all pesticides.

The SSGWM study is designed to provide information on the level of ground-water

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contamination that may arise from the use of a pesticide and thereby determine what use restrictions or other measures might be needed to prevent or otherwise mitigate ground-water contamination (*3*). USEPA requires these studies when the basic environmental fate studies required for registration indicate that the pesticide and/or its degradates of concern have a combination of mobility and persistence characteristics that could lead to enough leaching under the intended use pattern.

Controlled studies conducted in chambers or closed-system monolith lysimeters readily allow for use of radiolabeled pesticide and, as a result, a ready determination of the mass balance (*4*, *5*, *6*, *7*). However, recovery of the radiolabel still must be followed by extraction, separation, and identification of the residues. Success in accounting for the applied material over the course of the study provides some measure of assurance that one is correctly identifying the importance of both leaching and degradation as dissipation processes. Although the SSGWM study design does not allow for direct mass balance determinations, it does provide a three-dimensional accounting of the pesticide fate in the vadose zone and the upper boundary of the saturated zone using a combination of soil cores, soil pore water samples (from suction lysimeters nested at different depths in the vadose zone), and shallow ground-water samples.

Pesticides generally cannot be radiolabeled in open field studies because of legal restrictions. However, to facilitate tracking of subsurface transport of residues, one can use a conservative tracer such as bromide to evaluate the relationship of pesticide leaching to water movement traced by the bromide. This chapter evaluates the extent to which mass accounting can be estimated in SSGWM studies and the implications of taking a mass accounting approach to evaluating the results of such studies.

Case Studies of Pesticide Mass Accounting in Small-Scale Ground-Water Monitoring Studies

This section examines results from three SSGWM studies. The datasets used for this paper were generated by random drawings from normal distributions around each of the original data points from the SSGWM studies. The mass recovery data are presented here as total residue recovery (in some cases degradation products are included). In all cases either or both the parent pesticide and its degradates were compounds with high soil mobility (K_ds much less than 1 ml/g) and high soil persistence (degradation half-lives of a few months or greater).

Each of the study sites discussed in this paper had loamy sand or sand texture soils generally with <1% organic matter throughout the vadose zone and shallow unconfined aquifers with a depth to the water table of 3 to 6 meters. Suction lysimeters could not be easily installed at a depth of more than about 4 meters, so at some sites there may have been a gap of a few meters between the deepest soil pore water sampling device (i.e., suction lysimeter) and the shallowest ground-water monitoring well. Sufficient irrigation or precipitation occurred at the study sites to result in significant ground-water recharge in the first several months after application (confirmation of this was provided by bromide tracer data, presented here only for the pesticide B study site).

Methods for Mass Balance Calculations. Several assumptions related the distribution of residues in the subsurface environment and the representativeness of samples had to be made to estimate a mass balance (Table I). These assumptions impact the accuracy of the mass balance calculations.

Table I. Implications of assumptions for or limitations of mass balance calculations.

Assumption/limitation	Error sources and Implications
Concentrations in samples are representative of surrounding matrix	If the sampling procedure yields a biased sample, then the mass recovered will not be estimated correctly.
The method does not account for pesticide residues adsorbed in soil horizons sampled with suction lysimeters (and not soil cores), since only soil pore water was analyzed with the lysimeters.	If significant pesticide was adsorbed below the depth at which soil cores were used for analyses, then the mass recovered would be underestimated. In the studies reviewed in this paper, the error arising from this assumption is expected to be small because the K_ds of leached compounds in subsoil were likely very small (<0.1).
Soil water content was near field capacity and all soil water contained equivalent concentrations of pesticide	At times of low percolation, soil water content may have been lower, resulting in overestimation of the mass recovered with suction lysimeters. Some soil water may not be available, and contain no pesticide residues.
Pesticide is distributed only over the dimensions of the treatment area down to the lowest screening depth of the monitoring wells. The distribution of the pesticide is laterally uniform over the treatment area and is essentially nonvolatile	The pesticide distribution may be more skewed to the downgradient portion of the field. Over time, a greater mass of the pesticide may move out of the treated area and below the zone of ground water sampled with the monitoring wells. Consequently, the accuracy of mass balance determinations may be decreased. Calculations will increasingly underestimate the remaining residues with time for highly mobile or volatile compounds that leave the site of application.

The general forms of the equations used for this paper are described below.

Mass and Percent Recovery for Top Meter of Soil :

Mass in top meter of soil at sampled time in mg $= A \times \sum_{i=1}^{i=n} \rho_i C_{si} \Delta z_i$

where
A = area of treated field in m^2
n = number of soil cores

ρ_i = bulk density of soil in core i in kg/m^3
C_{si} = concentration in bulk soil in core i in mg/kg soil
Δz_i = core length in m
$\sum_{i=1}^{i=n} \Delta z_i$ = maximum depth to which soil cores are taken (generally 1 m)

%Recovery for mass in top m of soil at sampled time $= [A(\sum_{i=1}^{i=n} \rho_i C_{si} \Delta z_i)/rA] \times 100 = [(\sum_{i=1}^{i=n} \rho_i C_{si} \Delta z_i)/r] \times 100$

where
r = application rate in kg/m^2

Mass and Percent Recovery for Soil Pore Water:

Mass in pore water at sampled time $= A\{\Theta_{w1} C_{pw1}(d_2 - d_1)/2 + \sum_{j=2}^{j=N-1} \Theta_{wj} C_{pwj}(d_{j+1} - d_{j-1})/2 + \Theta_{wN} C_{pwN}[D - (d_N + d_{N-1})/2]\}$

where
A = area of field in m^2
N = number of lysimeters at different depths
Θ_{w1} = water content (m^3/m^3) for soil surrounding lysimeter 1 (the most shallow lysimeter), generally estimated at field capacity (approximately 0.1 for the sandy soils used in the studies)
C_{pw1} = concentration in pore water extracted by lysimeter 1 (the most shallow lysimeter) in mg/m^3
d_1 = depth of lysimeter 1 (the most shallow lysimeter) in m
d_2 = depth of lysimeter 2 (the next one below lysimeter 1)
Θ_{wj} = water content (m^3/m^3) for soil surrounding lysimeter j.
C_{pwj} = concentration in pore water extracted by lysimeter j in mg/m^3
d_{j+1} = depth of lysimeter j+1 (the next one below lysimeter j) in m
d_{j-1} = depth of lysimeter j-1 (the next one above lysimeter j) in m
Θ_{wN} = water content (m^3/m^3) for soil surrounding lysimeter N (the deepest lysimeter)
C_{pwN} = concentration in pore water extracted by lysimeter N (the deepest lysimeter) in mg/m^3
D = depth from the soil surface to the top of the aquifer in m
d_N = depth of lysimeter N in m
d_{N-1} = depth of lysimeter N-1 (the next one above lysimeter N) in m

%Recovery for mass in soil pore water at sampled time =
[(mass in pore water at sampled time)/rA] x 100%

Mass and Percent Recovery for Ground Water:

Mass in ground water at sampled time in mg = $\phi A \sum_{k=1}^{k=N'} C_{GWk} \Delta s_k$

where
ϕ = porosity, m^3/m^3
N' = number of depth-nested wells
C_{GWk} = concentration in ground water from screen k in mg/m^3
Δs_k = height of screen for well k in m that is fully in the saturated zone

%Recovery for mass in ground water at sampled time = $[\phi A \sum_{k=1}^{k=N'} C_{GWk} \Delta s_k / rA] \times 100 = [\phi \sum_{k=1}^{k=N'} C_{GWk} \Delta s_k / r] \times 100$

Total Percent Recovery:

Total % recovery at sampled time = (% recovery soil core) + (% recovery soil pore water) + (% recovery ground water)

More thorough data collection could allow for more refined forms of the above equations. Among the additional data that could be collected to further facilitate mass balance estimations are:

1. Monitoring for pesticide residues outside the treatment area (e.g., in downgradient wells), to facilitate estimation of the mass of pesticide moving laterally out of the treatment area with time.
2. Determination of available soil water content with depth and time, enabling more accurate estimation of the mass of pesticide recovered with the soil pore water samples collected with suction lysimeters.
3. Determination of partition coefficients of the pesticide and degradates of interest with depth in the profile (to facilitate quantitative estimation of the adsorbed portion of the pesticide residue not detected with soil pore water samples collected with the suction lysimeters).
4. Collection of pesticide vapors leaving the area or drift not reaching the soil inside the treated area.

Results and Discussion of Case Studies.

Mass Balance of Pesticide A. The residues of pesticide A dissipated from the surface soil layer within a few months but were detected in the vadose zone and ground water for a much longer time (Figure 1). Rapid dissipation from surface soil can reflect either rapid degradation, rapid leaching, volatilization losses, or decreasing extraction efficiency from the soil samples over time (which is a more likely explanation for less mobile compounds). More rapid degradation of pesticides in surface soil layers than in subsurface soil layers is a common phenomenon (*8*, *9*, *10*) and is a quite plausible explanation for the observed dissipation pattern. Volatilization losses of 30 to 60% have been reported for pesticides with vapor pressures as low as 10^{-7} mm Hg at 25 C (*11*, *12*) and pesticides have been detected in the atmosphere and in rainwater far from the site of application (*13*, *14*, *15*). Alternatively, it could be that residues in the deeper horizons were not efficiently intercepted with the soil water and ground water samples at any sampling interval (which could occur if, for example, adsorption increased substantially over time and the adsorbed residues were not extracted with the suction lysimeters). In any case, the results demonstrate that pesticide A was particularly persistent in deeper soil layers and ground water. Consistent with this hypothesis is the fact that 14% of the residues of pesticide A reached ground water within 2 months after application and persisted at detectable concentrations in the upper portion of the aquifer beneath the treatment area for approximately two years (only mass recovery estimates for up to 16 months after application are given in Figure 1). Pesticides that degrade only in surface horizons and not in subsoil normally degrade by microbiological processes only (*16*, *17*).

Half-life calculations provide further support for persistence of pesticide A in subsurface layers. For example, if the pesticide degradation half-life was consistently near one month in all soil layers (the measured dissipation rate of the pesticide from the upper meter of soil), then only a one in two million fraction of the amount applied would remain undegraded after two years (because more than 20 half-lives would be included in the two-year period). Therefore, with a consistent half-life of about one month it would be impossible to find detectable concentrations of pesticide A by 1 to 2 years after application.

An important feature of the data is that a substantial percentage of the applied pesticide (up to 35%) was recovered from the lower part of the vadose zone and ground water over a several-month period (Figure 1). This is one major advantage of SSGWM studies - direct determination of the impact of a known amount of pesticide use may have on ground-water resources. Recovery at the later sampling dates might have been improved if the mass of pesticide moving off-site could have been quantitated (in some SSGWM studies residues have been detected in downgradient wells outside of the treatment area). Accurate estimation of the mass of residues moving off-site would, however, require an extensive network of downgradient wells and a very sensitive analytical method since concentrations decline as residues diffuse over a larger area.

Mass Balance of Pesticide B. The residues of pesticide B had a surface soil layer dissipation half-life of approximately 60 days for the first few months after application (Figure 2). However, examination of the total recovery from soil water, ground water, and surface soil samples leads to the conclusion that pesticide B was more persistent than is evident from this dissipation half-life. By three months after application, more pesticide was recovered in soil water samples from the lower part of the vadose zone (25%) than in the soil cores from the top soil layer (15%). A spike of pesticide B in ground water occurred approximately four months after application (45%), and the estimated recovery of applied pesticide peaked above 80%. This suggests significant inefficiency in tracking the movement

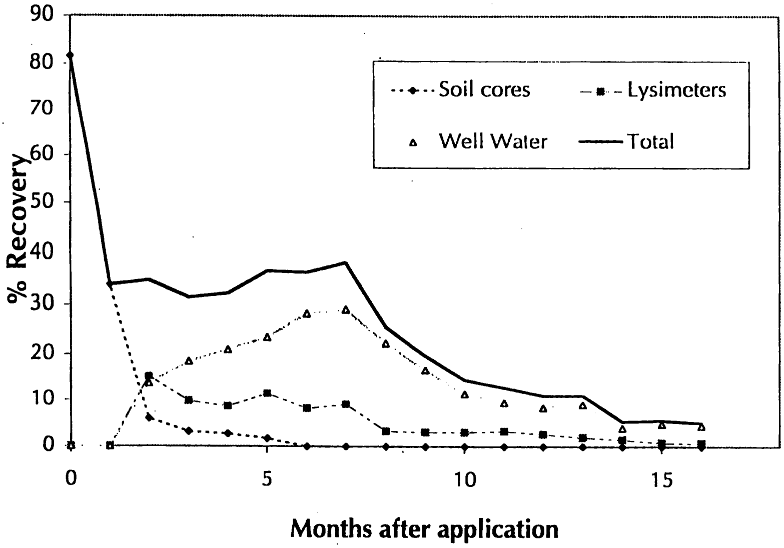

Figure 1. Estimated recovery of pesticide A from soil cores, soil-pore water, and ground-water samples. In this and Figures 2 and 3, soil core values reflect recovery from analysis of soil cores to a depth of up to one meter, soil-pore water samples were taken with suction lysimeters installed at various depths in the vadose zone (for example, 1, 2, 3, and 5 meter depths), and ground-water samples were taken from wells screened in approximately the upper 1.5 to 3 meters of a surficial aquifer.

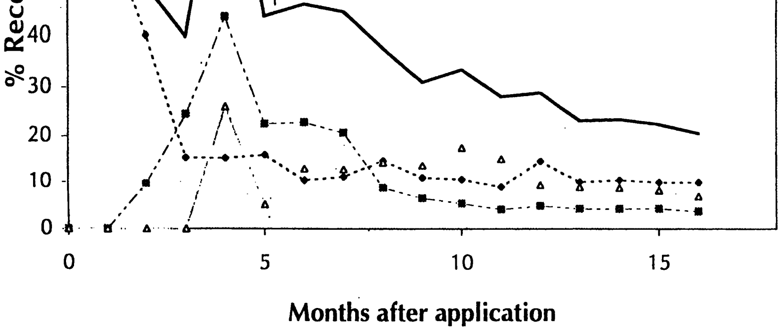

Figure 2. Estimated recovery of pesticide B from soil cores, soil-pore water, and ground-water samples.

of pesticide B through the vadose zone just prior to breakthrough into ground water. The bromide tracer recovery even more abruptly dropped at the 3-month sampling interval (Figure 3). These data show that a very thorough subsurface sample scheme and detailed weather data are necessary to track the mass of pesticide leaching over time when leaching occurs relatively rapidly such as was the case in this study. Temporary loss of recovery might occur if a large gap (vertically or perhaps laterally) in space between the deepest soil pore-water sampling station and the shallowest ground water sampling station exists.

After the first detections in ground water, recovery of pesticide B gradually declined over the next several months, but was still nearly 30% one year after application (the overall gross dissipation half-life was therefore slightly greater than 6 months, Figure 2). Some of this recovery loss could have been due to degradation or volatilization of pesticide B, but it is also possible that there was movement of pesticide B residues off-site or into deeper ground water.

Pesticide B, after its initial rapid dissipation in the surface soil layer, was very persistent from approximately 3 months after application, with the residues recovered remaining steady at 10 to 15% of applied. This may reflect lower rainfall and irrigation levels (reducing leaching), lower soil temperatures (reducing the degradation rate), and/or possibly increased sorptivity of the pesticide to soil clay and organic matter over time (reducing extraction efficiency).

Mass Balance of Pesticide C. Pesticide C was applied three times over a period of several months (Figure 4). Consequently, interpretation of mass recovery is more difficult. Recovery spikes were observed immediately after the second and third applications. Subsequent to each application, recovery percentages were calculated on the basis of the sum of the previous applications.

Within a few months after the final application of pesticide C, the residues were predominantly in the soil water and ground water, with residues in soil cores declining to near the minimum detection limit. This study demonstrates temporary reductions in mass accounting as apparent soil residue levels declined after each of the three applications. The pattern is similar to that observed with pesticide A except that the estimated mass recovery of pesticide C did eventually begin to increase again as more residues were detected with the suction lysimeters and ground-water monitoring wells beginning approximately 11 months after application. Therefore, either the mass of pesticide residues remaining in the soil profile in the early months was underestimated (presumably because of declining extraction efficiency of the analytes from soil since the recoveries dropped rapidly after each application) or the mass recovery in the later months was overestimated (because the residues detected were representative of a lower volume of soil pore-water or ground water than estimated).

The recovery data show that pesticide C residues were extremely persistent. Estimates of mass recovery were still between 60 and 80% of the cumulative applied material up to 16 months after application (Figure 4). This suggests that one or more of the analytes can persist for years with dissipation (and degradation) half-lives of significantly more than one year in the vadose zone and ground water.

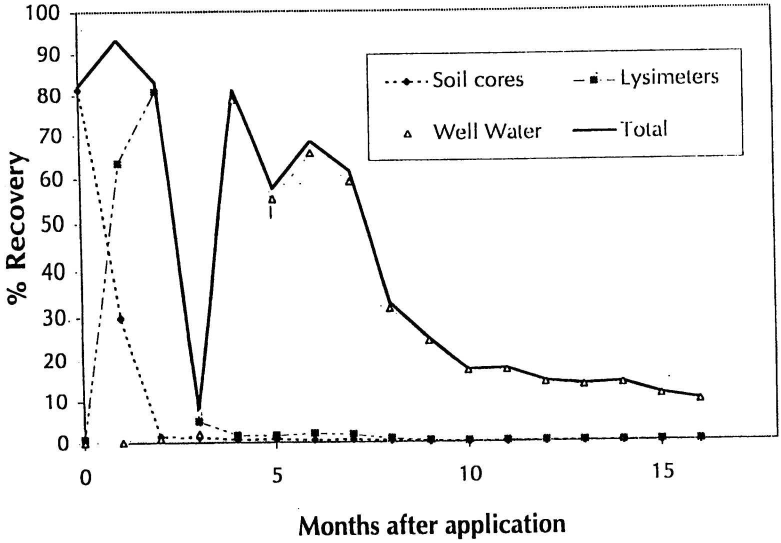

Figure 3. Estimated recovery of bromide (study with pesticide B also applied) from soil cores, soil-pore water, and ground-water samples.

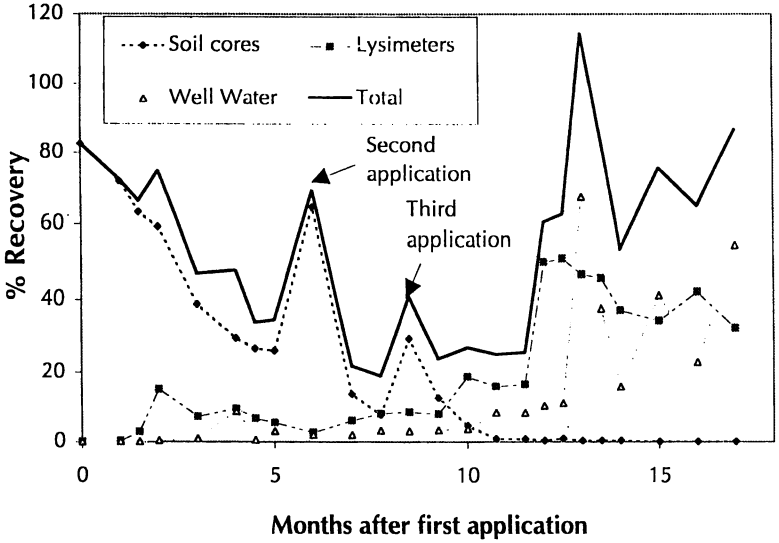

Figure 4. Estimated recovery of pesticide C from soil cores, soil-pore water, and ground-water samples.

Impact of Spatial Variability in Soil Characteristics and Hydrology on Mass Balance in Field Studies

Thurman et al. (*18*) have reported in this volume on how soil properties related to pesticide transport (e.g., hydraulic conductivity) can vary greatly over a distance of a few meters, even in sandy soils with apparently uniform properties. Although each of the case studies discussed in this chapter were conducted in soils with sand or loamy sand textures, significant variation in the amounts leaching occurred over the course of the study. Generally, the mass of pesticide detected in soil water varied by up to a factor of five between replicate lysimeters at a given depth. The current USEPA guidelines for SSGWM studies require that spatial variability in leaching be examined using a minimum of eight suction lysimeter clusters (each including sampling devices at three or four different depths) and eight monitoring well clusters be installed in the treatment area of approximately one hectare in size (*3*). In monolith lysimeter studies, additional variations in pesticide leaching may arise from artifacts of the enclosure around the treatment area (*18, 19*). The main advantage with a well-designed SSGWM study with quality control of sampling and analytical procedures is that, without the potential for such artifacts, the data from multiple sampling sites provide information on variations in the mass of pesticide leaching per unit area under field conditions.

Comparison of Mass Balance or Accounting Issues in SSGWM and Monolith Lysimeter Studies

Monolith lysimeter studies are conducted in a confined column or chamber, facilitating total recovery of applied pesticides that are not lost into the atmosphere (and. in addition, the lysimeter experiment can be adapted to recover volatilized residues). However, the full significance of ^{14}C recovery data is not easily interpreted unless most of the residues confirmed through radiometric analyses can also be separated and identified. In the three examples of pesticide residue accounting for ground-water monitoring studies discussed in this chapter, mass recovery of pesticides was improved when soil, soil pore water, and ground water analyses were considered together. This type of field mass balance approach provides additional information on the extent of scale-dependent leaching and confirms the importance of dissipation pathways.

SSGWM and other field leaching studies have primarily relied on either analysis of soil core depth increments or of soil-pore water samples collected with suction lysimeters buried at various depths. The reliability of residue measurements with soil cores and traditional soil sampling procedures has been questioned because great spatial variability in pesticide residues may make it very difficult to obtain a representative sample (Nelson, E.M., An Investigation into the Effects of Heterogeneity on Subsurface Flow and Transport, M.S. Thesis, Univ. of North Carolina, Chapel Hill, 1993). Another limitation of using analyses of soil cores to track leaching is that analytical methods usually cannot be made as sensitive and accurate as needed.

In contrast, soil water samples typically present less matrix interference problems and therefore allow for greater detection sensitivity. The suction lysimeters used in SSGWM studies present their own sampling problems. For example, the lysimeters may not consistently collect sufficient soil water for pesticide residue analysis. An assumption must be made that the soil water sample is representative of the surrounding soil and that the presence of the suction lysimeters as sample collection devices does not alter the flow of the soil water.

Monolith lysimeter studies, because they can be designed to directly examine pesticide dissipation by various routes, provide a way to determine how much of the dissipation of a highly mobile pesticide under field conditions is due to degradation and how much is due to leaching (assuming that edge effects of the lysimeter do not significantly affect leaching). Pesticide A residues showed a rapid reduction in the percentage of the applied pesticide that was accounted for in the first several weeks after application. Using monolith lysimeter studies in conjunction with this SSGWM study would help confirm the reason for the rapid recovery loss in the first several weeks after application - whether it was really due to initially rapid degradation of pesticide A or to analytical problems or other dissipation processes such as volatilization. Another way in which monolith lysimeter studies could be used to supplement SSGWM studies would be to provide an opportunity to evaluate the behavior of the pesticide under a variety of environmental conditions. For example, a series of monolith lysimeters exposed to different temperatures could be used to answer the question: Does the amount of pesticide A leaching decrease significantly as the temperature is raised? If it does, this provides supporting evidence that the initial loss of pesticide A recovery in the SSGWM study was because the degradation or volatilization was relatively rapid and the surface soil layer was relatively warm during this period. Other factors that can be examined at a single study site with multiple lysimeters include various simulated precipitation or irrigation schemes, cropping or fertilization schemes, soil pH, or even use in different soil series.

The recovery data for each pesticide (Figures 1, 2, and 4) illustrate the potential for inefficiencies of the SSGWM study sampling program in accounting for the mass of the applied pesticide that leaches. In each case there appeared to be, at least temporarily, some increase in the overall mass of pesticide detected once significant concentrations started appearing in ground water. As previously discussed, these recovery "gaps" may be due to poor recovery from the soil matrix in the case of bulk soil analyses of soil cores or to substantial gaps between the lowest lysimeters and the shallowest monitoring wells. Although monolith lysimeters do not provide direct confirmation of the amount of the pesticide reaching ground water, they can provide information on whether it is possible for significant quantities of pesticide to reach ground water (because these studies provide an opportunity for precise determination of pesticide quantities in leachate) (*20, 21*).

Summary

These case studies demonstrate that there can be substantial added value for pesticide dissipation studies from monitoring, in addition to residues in the topsoil, the subsurface movement of the pesticide and its degradates. This is particularly true for highly mobile and persistent compounds. Since the small-scale prospective ground-water monitoring study used to support registrations of pesticides in the United States is conducted under normal (largely uncontrolled) field conditions, all routes of dissipation may not be fully identifiable. But in each of the examples given in this paper, analysis of soil water in the vadose zone and of shallow ground water led to greatly improved recoveries at later sampling intervals over analysis of soil cores alone. Recoveries were generally in the order of pesticide C residues > pesticide B residues > pesticide A residues, which is the order of the relative soil persistence of each of these compounds (data not presented). All three compounds were more persistent in the lower part of the vadose zone and in ground water than would be predicted from studies evaluating dissipation or degradation rates in surface soil layers alone, a phenomenon which has been reported with a number of pesticides recently (*8*, *9*, *10*). Field dissipation behavior can not be completely addressed in the same way with monolith lysimeter studies, because their hydrology is disconnected from the lower part of the vadose zone and ground water. It has been reported that soil column lysimeters equipped with leachate collectors had 7% less downward movement of pesticides than lysimeters with no collectors and the difference was attributed to the interruption of capillary action (*21*). Monolith lysimeter studies have not been consistently used to predict ground concentrations (*22*).

Given the requirement in the United States to estimate ground water concentrations and especially drinking water exposure levels for individual pesticides and pesticide classes with geographic specificity, the small-scale prospective ground water monitoring study provides invaluable regulatory information which cannot at the current time be readily obtained with monolith lysimeter studies alone. However, small-scale prospective ground-water monitoring studies and monolith lysimeter studies can be used in combination to provide a more comprehensive picture of the portions of the use area for a pesticide where ground water contamination problems are more likely.

Disclaimer

The views expressed in this paper are entirely the authors', and do not represent or reflect the policy of the Environmental Protection Agency or any other entity of the United States government.

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Chapter 18

Lysimeter Data in Pesticide Authorization

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The assessment of the mobility of plant protection products in soil is a very important part within the authorization procedure for pesticides in the Federal Republic of Germany.

In recent years lysimeter studies have been proven to be the best methods to assess the probability of pesticides entering into ground water. For substances with a DT_{50} value of more than 21 days and an adsorption constant Koc of less than 500, computer-aided model calculations at realistic worst case conditions are first conducted. If a concentration of 0.1 μg/l or more is calculated, lysimeter studies have to be carried out. An authorization of the plant protection product is only granted if the concentration of the active substance in the leachate is less than 0.1 μg/l averaged over one year. The lysimeter concept was also adopted by the EU Directive 91/414/EEC where in special cases lysimeter or field studies for the assessment of the mobility of active substances are required. In the last few years lysimeter studies were conducted for more than 40 active substances within the German authorization procedure.

First an overview on the role of lysimeter studies within the authorization procedure and the requirements for the necessity of carrying out such studies shall be given.

To prevent an unjustifiable contamination of ground water, within the authorization procedure of plant protection products in Germany, information on the degradability and mobility of the active substance in soil is needed to be able to assess the possibility of ground water contamination.

The basis for these requirements is the German Plant Protection Act of 1986 which states in Article 15 that an authorization can only be granted if the plant protection product "...does not have any harmful effects on human and animal health or on ground water.".

In The Lysimeter Concept; Führ, F., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 1998.

Unfortunately, the legislator failed to give a definition of the term "harmful effects". Therefore, in 1989 the Federal Biological Research Center for Agriculture and Forestry (BBA) decided, in agreement with the Federal Environmental Agency (UBA), that a harmful effect must be assumed, and that therefore an authorization must be refused, if in the investigation of the mobility of the active substance it seems that concentrations in ground water of 0.1 μg/l or more could be expected.

This decision was confirmed within two court proceedings at the Administrative Court in Braunschweig in 1990, where it was said that "the entry of an active substance into ground water then leads to inadmissible effects if after the proper use of the respective plant protection product, the limit of the Drinking Water Ordinance of 0.1 μg/l is reached or exceeded". The assumption as to what concentrations of pesticides in ground water could be expected is based on results of lysimeter studies.

Advantages of Lysimeters

Among the different methods for the estimation of the mobility of active substances in soil, lysimeter studies are regarded up to now to be most reliable, because such trials enable the use of undisturbed soil cores and, of particular importance, the application of radioactively labelled test material. The advantages of lysimeter studies versus laboratory leaching studies are obvious (*1*):

- They are performed under real environmental conditions, e. g. natural precipitation, sunshine, air and soil temperatures.
- Use of a natural soil profile instead of repacked soil columns in the laboratory.
- The possibility of cultivation of the lysimeter surface according to good agricultural practice.
- Microbially active soils; soils for laboratory studies are often air-dried prior to use.
- Realistic soil depth thus taking into account the change in the degradation rate with downward movement of the active substances.

Even in comparison with field studies there are considerable advantages:

- The possibility of using radioactively labelled test material. The use of radioactively labelled material in field studies is usually prohibited.
- The possibility of comparison of different soil types.
- An easy and comparable study management, e. g. the location of different lysimeters at the same facility ensures identical management practices.
- The possibility of artificial irrigation.
- The sampling of the total leachate; all water draining through the profile can be collected for analysis thus allowing a tentative mass balance

Necessity of Lysimeter Studies

However lysimeter studies are not necessary in every case in the course of the German authorization procedure. The decision on whether such studies are necessary or not might be made by using the flow diagram shown in Figure 1.

If the degradation rate of the respective active substance shows a DT_{50} value (lab.) of less than 21 days and an adsorption constant K_{oc} of more than 500 with regard to the safety of ground water, an authorization can be granted, because the probability of a penetration into deeper soil layers by normal leaching events would be minimal. If the DT_{50} value exceeds 21 days and the K_{oc} value is less than 500, computer-aided model calculations have to be conducted first, taking into account realistic worst case conditions. Within the Member States of the EU, different calculation models are used, e.g. in the Netherlands the PESTLA model is preferred, whereas in Germany the PELMO model is regarded to be the most appropriate model. In most cases, the calculation covers a period of 10 years.

If the PELMO calculation shows a simulated concentration of 0.1 µg/l or more in ground water for at least one year, lysimeter studies have to be conducted. It must be stressed that modelling results are used as triggers for the necessity of lysimeter studies and **not** as cutoff triggers.

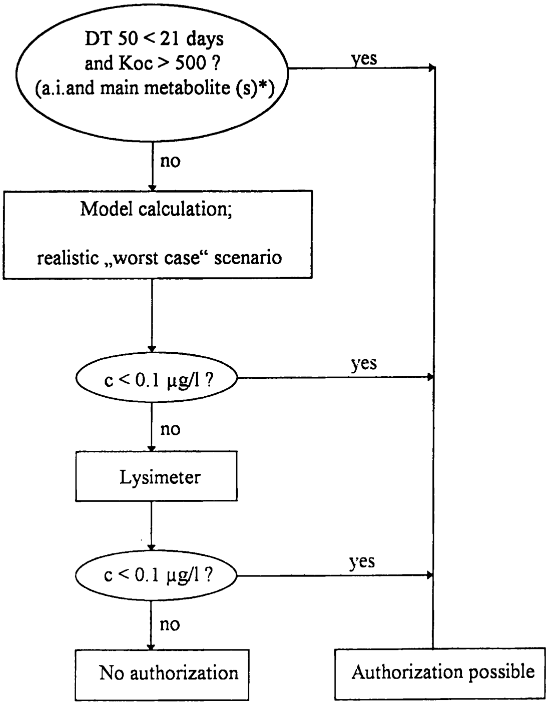
A comparison between lysimeter and PELMO results (on the basis of 39 lysimeter cores, 14 active substances, 1 metabolite) which was conducted by order of the German Agrochemicals Association (IVA) and the Federal Environmental Agency (UBA) (*2*) showed that the PELMO calculations are appropriate to estimate the probability of ground water contamination.

Lysimeter Studies

The conditions under which lysimeter studies should be conducted are laid down in a BBA-Guideline (*3*). In these experiments, an undisturbed soil core of 1.0 - 1.2 m depth and a surface of 0.5 - 1.0 m^2 should be used. The soil should be a light sandy soil with a content of at least 70 % sand, at the most 10 % clay and not more than 1.5 % organic carbon.

The preparation of the active substance which should be radioactively labelled is applied in the highest intended amount and at the intended time. A precipitation rate of at least 800 mm per year must be maintained, possibly by irrigation. The experiment is conducted over a period of at least 2 years but in some cases up to 4 years. During this time, the lysimeter is cultivated according to good agricultural practice.

The percolated water is sampled from time to time and analyzed for the contents of total radioactivity, parent compound, metabolites and unidentifiable radioactive residues. At the end of study, the soil core from the surface to the bottom is divided into 10-cm layers, and each layer is also analyzed for total radioactivity, parent compound, metabolites and bound residues, thus illustrating the distribution of the different fractions in the whole soil core and giving additional information about the degradability and degree of adsorption of the compound and its metabolites to soil particles. According to the lysimeter results submitted up to now, it seems that only in the upper 20-cm soil layer was the concentration of extractable radioactivity high


DT 50 < 21 days
and Koc > 500 ?
(a.i.and main metabolite (s)*)
yes
no
Model calculation;
realistic „worst case" scenario
c < 0.1 µg/l ?
yes
no
Lysimeter
c < 0.1 µg/l ?
yes
no
No authorization
Authorization possible

* main metabolite > 10 % at any time during the study
c = concentration in leachate

Decision-making flow diagram for evaluation of the potential of a pesticide or its metabolites to move into groundwater enough to identify the active substances and sometimes their metabolites, too. In the deeper soil layers the concentration of extractable radioactivity normally was so low that a separation into parent pesticide and metabolites was not possible.

Assessment of Lysimeter Results

A question of great importance is the assessment of lysimeter results. In Germany this assessment is conducted as follows (Figure 1):

If the concentration of a pesticide in the lysimeter percolates reaches or exceeds 0.1 µg/l, averaged over one year, no authorization is granted. Contrary to the PELMO calculations, in this case **it is a cutoff value**.

Since 1988 lysimeter studies for more than 40 pesticides, mostly herbicides, have been conducted (Table I):

Table I. Pesticides for which Lysimeter Studies were Conducted

Amidosulfuron	Kresoxim-methyl
Bentazone	Linuron
Carbofuran	MCPA
Carbosulfan	Mecoprop
Chloridazon	Mecoprop-P
Chlortoluron	Mefenpyr
Clopyralid	Metalaxyl
Cyanamide	Metam-Na
2,4-D	Metazachlor
Dazomet	Metabenzthiazuron
Dicamba	Metobromuron
Dichlobenil	Metosulam
Dichlorprop	Metribuzin
Dichlorprop-P	Monolinuron
Dimethenamid	Pendimethalin
Dimethoate	Phenmedipham
Ethofumesate	Propoxur
Fenpropidin	Propyzamide
Fluroxypyr	Pyridate
Flurtamone	Quinmerac
Fluquinconazole	Simazine
Glufosinate	Terbuthylazine
Isoproturon	Triclopyr

In every case no harmful effects on ground water could be expected, i.e. the concentrations in the percolates were below 0.1 µg/l, averaged over one year, or even not detectable.

Depending on a limit of determination of 0.01 to 0.04 µg/l, in 80 % of the cases no pesticides were detectable in the lysimeter leachates averaged over one year. In the other cases the respective compounds were found in the following ranges of concentrations (limit of determination always < 0.01 µg/l)

0.01 - 0.03 µg/l :	~ 4 %
0.03 - 0.05 µg/l :	~ 8 %
0.05 - 0.1 µg/l :	~ 8 %
> 0.1 µg/l :	0 %

From these positive results, it could be concluded that lysimeter studies will always have positive results, i. e. never exceeding the 0.1 µg/l value in the leachate, for every active substance, but it isn't like that. Because the applicants know that an authorization is not granted if in a lysimeter study the 0.1 µg/l value is exceeded, they may refrain from submitting an application for authorization for pesticides that are too mobile and too persistent.

Metabolites and Nonidentifiable Radioactivity

In contrast to the positive results for the parent compounds, metabolites and nonidentifiable radioactivity (NIR) often were detected in concentrations above 0.1 µg/l. Table II shows typical results from two lysimeter studies:

Main metabolites in Germany (and in the EU) have been defined conventionally to be those degradation products which occurred in degradation studies in concentrations of 10 % or more, relative to the initial radioactivity, at any time of the study. If main metabolites or NIR's are found in the lysimeter percolate in concentrations of 0.1 µg/l or more - averaged over one year - an authorization is only granted if it can be shown that these concentrations are not harmful to human and animal health, nor to aquatic organisms (fish, daphnia, algae). If the No Observed Effect Concentrations (NOEC's) are 1000 times higher than the concentrations of metabolites in the percolates, an authorization can be granted. Examples are shown in Table II.

Unfortunately, not all problems regarding possible water contamination can be solved by lysimeter studies, particularly the problem of fast flow processes under field conditions, e.g. through holes from roots or worms, and particularly through soil cracks which may be formed in periods of warm and dry weather. These problems cannot be solved within the authorization procedure nor by experiments. This is a political question. One can either accept such potential contaminations or one has to ban almost all agricultural chemicals.

Furthermore, objections are sometimes raised that lysimeter studies cannot cover leaching in all types of soil under agricultural use. However, the conditions used for lysimeter studies in the German authorization procedure are "realistic worst case conditions", and we believe that these results cover the majority of situations with regard to different soil types and weather conditions in Europe.

With the procedure practised in Germany regarding the problem of ground water, the problem is considered to be under control, since pesticides which may reach

Table II. Exemplary Lysimeter Results of Pesticides and their Main Metabolites

Year	Lysimeter (Concentration in the Percolate µg/l)		
	Pesticide	Main Metabolite 1	Main Metabolite 2
Ø 1. Year	0.06	2.35	0.04
Ø 2. Year	0.05	0.79	0.74
Ø 1. + 2. Year	0.05	1.42	0.45

Ecotoxicity (NOEC-values)	**Metabolite 1:**	**Daphnia magna**	**100 mg/l**
		Rainbow trout	**100 mg/l**
	Metabolite 2:	**Daphnia magna**	**25 mg/l**
		Rainbow trout	**5 mg/l**

Year	1. Lysimeter (Conc. Percolate µg/l)			2. Lysimeter (Conc. Percolate µg/l)		
	Pesticide	**Metabolite 1**	**Metabolite 2**	**Pesticide**	**Metabolite 1**	**Metabolite 2**
Ø 1.	< 0.05	1.7	0.3	< 0.05	2.7	0.9
Ø 2.	< 0.05	0.7	0.1	< 0.05	4.0	1.0
Ø 3.	< 0.05	0.2	0.1	< 0.05	0.2	0.2
Ø1. + 2. + 3.	< 0.05	1.2	0.2	< 0.05	2.6	0.7

Ecotoxicity (NOEC-values)	**Metabolite 1:**	**Algae**	**200 mg/l**
		Daphnia magna	**<100 mg/l**
		Rainbow trout	**100 mg/l**
	Metabolite 2:	**Daphnia magna**	**< 95 mg/l**
		Rainbow trout	**87 mg/l**

the ground water table will hopefully be discovered during testing and will thus not be authorized.

Lysimeter studies are not only useful to investigate the leaching behaviour of a pesticide but also to determine the possibility of its accumulation in soil under field conditions as a result of repeated application of the respective pesticide over a period of several years.

The Situation within the Framework of European Legislation

With Council Directive 91/414/EEC, the basis for the harmonization of the examination and assessment of plant protection products in the EU was established.

The directive is based on the following principles:

- The authorization of plant protection products remains under the responsibility of the Member States.
- An authorization by a Member State is possible if the active ingredient of the respective plant protection product has been examined according to the community procedure and is found to be acceptable. Such active substances are listed in Annex I of the Directive (positive list). The requirements for the documents to be submitted for the inclusion in Annex I are described in Annex II for the active substance and in Annex III for at least one preparation.
- The assessment of the plant protection products has to be performed by the national authorities according to Annex VI (Uniform Principles) of the Directive.

- To simplify the free trade of products and to reduce trade distortion, a procedure of mutual acceptance of authorizations has been introduced.
- The (mostly well known) active substances which are already contained in authorized pesticides are re-evaluated by a special program in which all Member States take part. About 800 active substances should be reassessed within the next 12 years.

Decision-making on the ground water problem resembles the German procedure, except that there are no clear trigger values defined as to whether lysimeter studies are necessary or not. It is stated that expert judgement is required to decide upon the necessity of lysimeter studies. Alternatively, field studies may be carried out.

In Annex VI of the EU Directive 91/414/EEC, the decision-making procedure is described. Up to now, a trigger value regarding possible ground water contamination is still in discussion, but it seems probable that in Annex VI the 0.1 µg/l value will also be adopted as the cutoff criterion. And so it is expected that in the future, the problem of ground water contamination will be solved in the whole of the EU; by means of lysimeter or perhaps field studies, pesticides which tend to migrate into ground water can certainly be identified and will not be authorized.

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Chapter 19

Comprehensive Tracer Studies on the Environmental Behavior of Pesticides: The Lysimeter Concept

Effects and Exposure Assessment

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Lysimeters using appropriate sizes and methodology has substantial potential to improve risk assessment. This potential for futural improvement of the basis for risk assessment includes, in addition to the assessment of the fate of pesticides in soils and groundwater contamination, comprehensive studies for efffects on flora, fauna and mesofauna as well as effects in the aquifer. Major use of lysimeters at present practically is limited to fate and leaching investigations. In the fate assessments mostly concentrations are considered, but the loading concept - with respect to critical loads - may be a complementary alternative. Practical use of lysimeters in pesticides registration basically is following a realistic worst case scenario concept. Generic sets of scenarios considering data statistics and experimental uncertainties would provide improved bases for comprehensive risk assessments and for variations in time at one site, as well as for variations in time and space for regions.

In the following, examples are given for other uses of lysimeters. The examples include one concerning accumulation in soil from multiple applications, one on lysimeter toxicity testing to improve the information on the ecotoxicological potential of residues in soil and examples on indirect use of lysimeter data for the estimation of exposure in different regions (sensitivity of regions for pesticides leaching).

Lysimeters and Exposure/Effects Assessment

Practical use of lysimeters in pesticides registration usually follows a scenario concept (realistic worst case) and therefore is not targeted to a exposure/effects assessment in a probabilistic sense (*1, 2, 3*). In addition, the broad potential of lysimeters for investigating a wide array of fate and also effects parameters is not regularly used. Lysimeters provide an excellent tool to elaborate information on the long-term

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ACS Symposium Series; American Chemical Society: Washington, DC, 1998.

accumulation of residues in soil including non-extractable residues, they provide a tool to assess the partitioning of residues in soil including the partitioning between biota and the soil matrix, they are feasible to elaborate information on effects on soil fauna, they may be used for plant uptake and plant metabolism studies to give just some examples. For all these questions the influence of soils and climates are reflected in the results. Consequently, they may be used for comprehensive exposure/effects assessment for specific sites additionally. As a result of the realistic worst case concept there may be more sensitive areas which are not included in the realistic worst case, and there are less sensitive regions for which the scenario provides an overestimation of risks.

Accumulation of Residues in Soil

The accumulation of residues in soil measured upon repeated applications in field plots and in lysimeters. As there is no dilution by horizontal movement in lysimeters as occurring in field plots, the measurement of the long-term accumulation by lysimeters provides again a more realistic information for the maximum accumulation. Figure 1 gives an example for this build up of soil residues over five years. The experiments were performed according to the BBA-Guideline. Despite some accumulation observed during the first three years, the conditions in the last two years were such, that the residues almost reached the level after the first year of application. Although the study was done over five years only it indicates, that for the herbicide under investigation there is low long-term continous accumulation (*4*).

The observations are different for the formation of non-extractable residues (non-extractable radioactivity after solvent and subsequent sodium hydroxide extraction). As can be seen from Figure 2, there is a continuous build-up of non-extractable residues during the experimental period for the same pesticide as investigated above and a steady state is not reached after 4 applications. For an assessment of the build-up of non-extractable residues in soil information on the identity of the measured radioactivity would be needed.

Effects of Contamination in Soil

As mentioned, lysimeters of the size discussed here have not been used so far for effects assessments of pesticides. Small size undisturbed soil columns occasionally, named lysimeters, are, however, a standard tool for the assessment of effects, especially on nutrient cycling. A study is ongoing in this Institute to investigate the feasibility of using outdoor lysimeters for effects endpoints. Figure 3 gives a comparison of a study on some biological endpoints in planted outdoor lysimeters as compared to large (1,8 m^3) closed laboratory reactors. The large laboratory reactors are included in the study as a fully controlled alternative. The experiments presented in Figure 3 are controls only without application of a pesticide, and changes in the

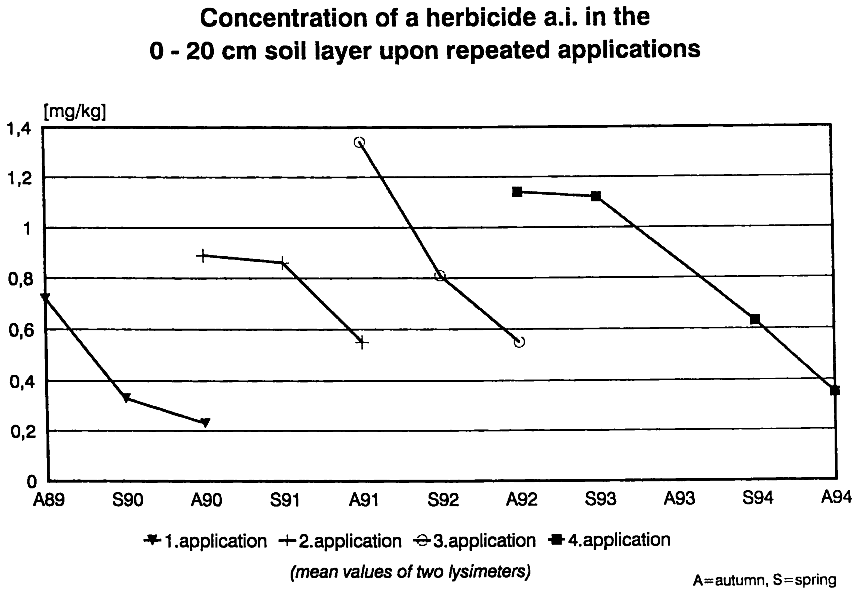


Figure 1: Concentration of a Herbicide A.I. in the 0 - 20 cm Soil Layer Upon Repeated Applications.

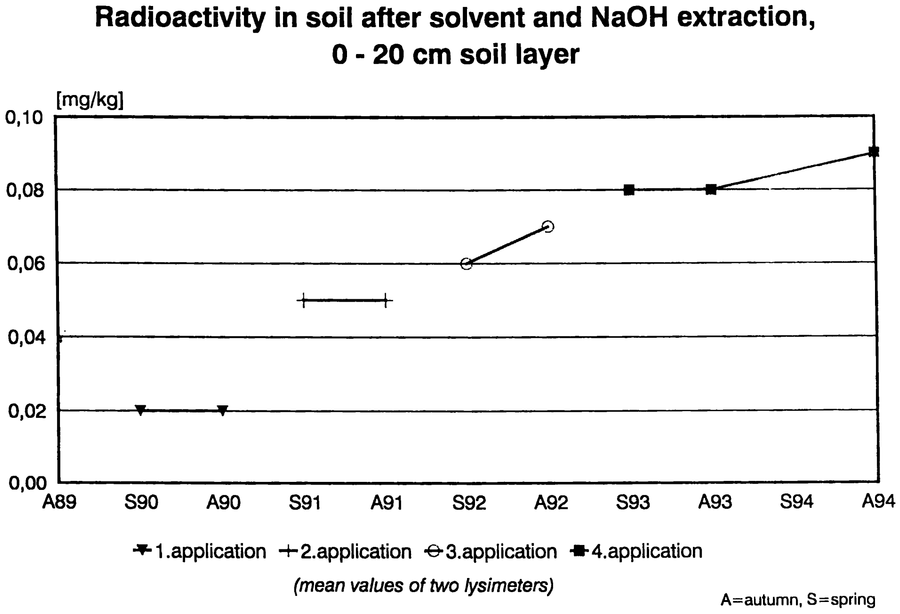


Figure 2: Non-extractable Radioactivity in Soil after Solvent and NaOH Extraction, 0-20 cm Soil Layer.

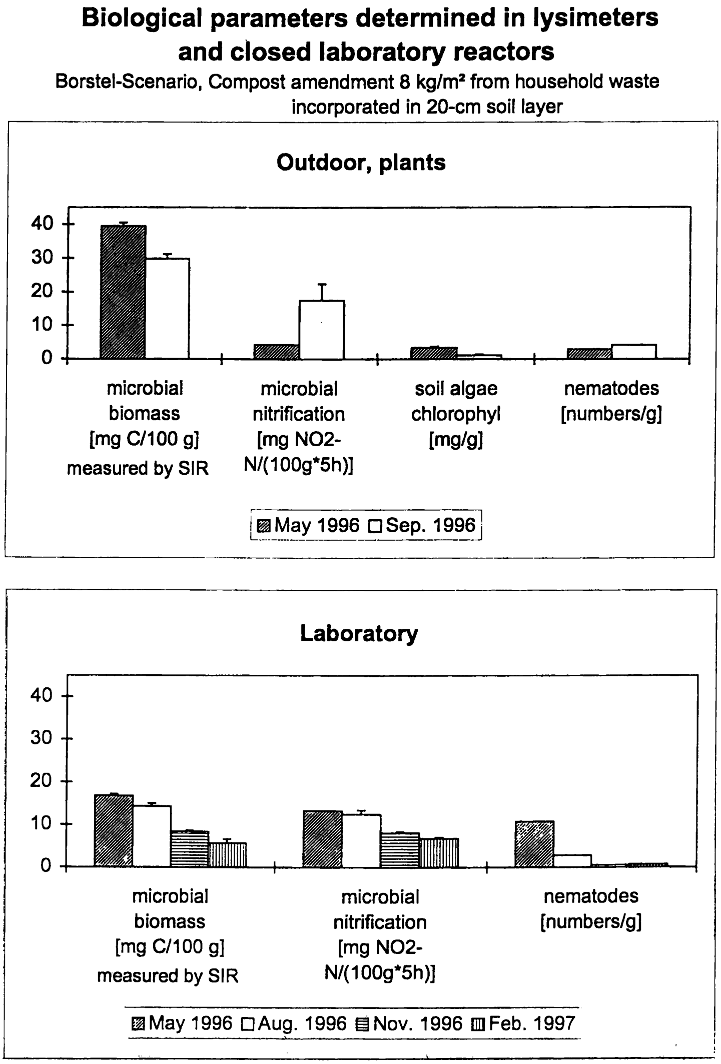


Figure 3: Biological Parameters Determined in Lysimeters and Laboratory Reactors - Both not treated with Chemicals.

biological response in the course of time therefore represent the depletion of the carbon source or nutrients, respectively (*4*).

Figure 4 shows the results for effects in parallel lysimeter studies using the contamination of composts as a stressor. Nitrification is a sensitive acute parameter whereas the others do not show significant effects. There are studies ongoing with pentachlorophenol, pyrene and di-ethyl-hexyl-phthalate. In order to investigate the long-term effects, these investigations are continued over an experimental time of 3 years (*4*).

There is at present much effort in many research groups to develop biological test batteries representing relevant endpoints in soils and waters. The emphasis for these ecotoxicological test batteries is on the development of in-vitro tests. These include also mode of action specific endpoints. The state of the art has recently been critically evaluated and summarized (*5*). Using this test battery will provide an important complementary tool for risk assessment of pesticides in soil. In order to avoid different handling of "samples" and assure identical exposure in the biological tests of the battery, lysimeters provide the optimum of investigation methodology. They are also the optimum tool for the validation of in-vitro tests with respect to ecological relevance.

The Potential Leaching Behaviour of Pesticides in different Soil-Climate-Regions of Germany

Since regional soil and climate properties are important in the control of the leaching processes, they are important to predict the fate of chemicals in soil. Relevant processes in soil are simulated e.g. in the model PELMO (*6, 7*). For the elucidation of regional differences in Germany, an estimation of infiltrating water was carried out for a total of 22 areas. The scenarios were based on a combination of the 12 most important soil regions in Germany (Figure 5), as defined by the German Federal Institute for Geosciences and Natural Resources (*8, 9*), and 9 climate areas represented by a meteorological station (Table 1, daily data for 30 years are available for each station) to estimate the infiltrating water for all scenarios.

The data for one soil region in each case represent a typical average scenario based on a weighted computation of several predominant soil profiles. The spatial inhomogeneity of soil structures and soil types are not further considered.

For each of the above mentioned soil regions the detailed profile data for the spatially mostly spread soil types are used to compute an average "synthetic" profile as basis for the modelling of pesticide leaching with PELMO. The soil properties of each surface layer in all regions are listed in Table 2.

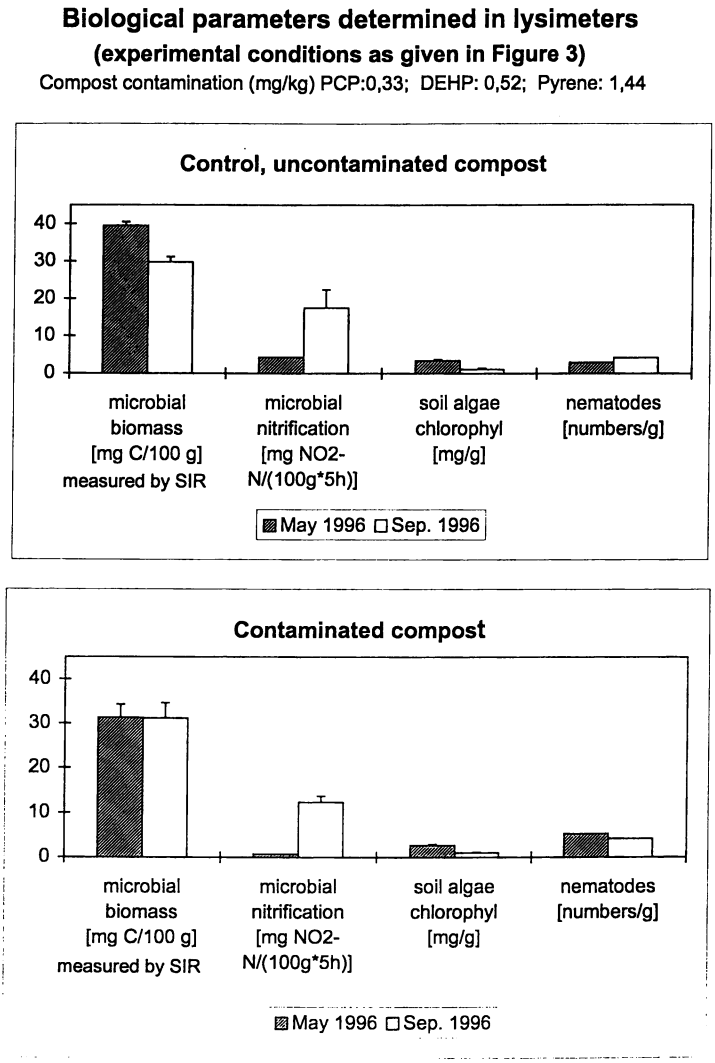
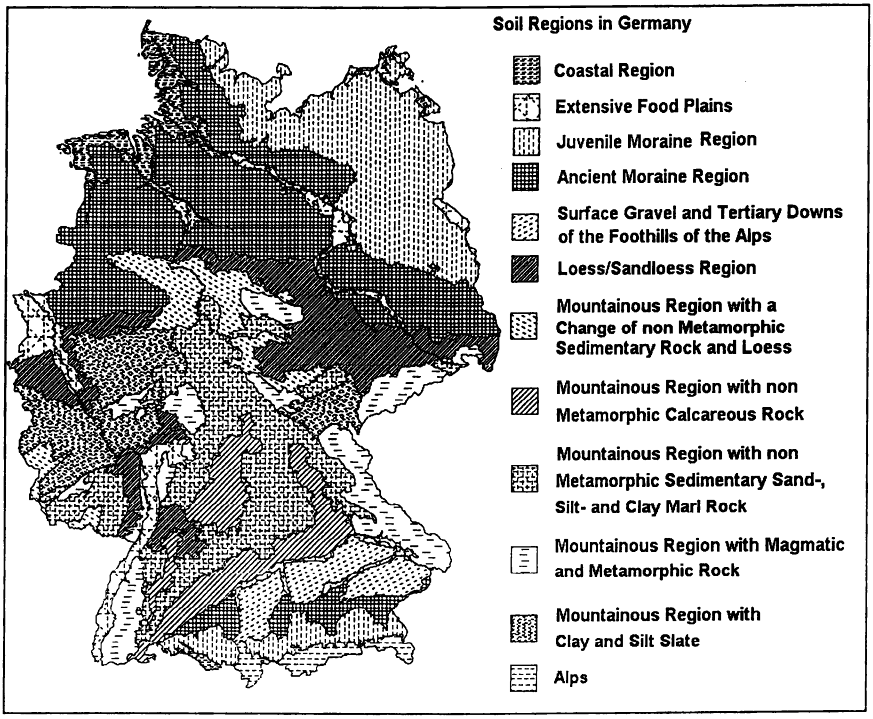


Figure 4: Effects of Compost Contamination on Soil Biota.


Soil Regions in Germany
Coastal Region
Extensive Food Plains
Juvenile Moraine Region
Ancient Moraine Region
Surface Gravel and Tertiary Downs of the Foothills of the Alps
Loess/Sandloess Region
Mountainous Region with a Change of non Metamorphic Sedimentary Rock and Loess
Mountainous Region with non Metamorphic Calcareous Rock
Mountainous Region with non Metamorphic Sedimentary Sand-, Silt- and Clay Marl Rock
Mountainous Region with Magmatic and Metamorphic Rock
Mountainous Region with Clay and Silt Slate
Alps

Source: BGR. Reproduced with permission from ref. 8. Copyright 1995 Hartwich et al.

Figure 5: The Most Important Soil Regions in Germany.

Table 1: Climate Regions of Germany

No.	Climate Area	Representative Site
1	North Sea coast, Baltic Sea coast of Schleswig-Holstein	Schleswig
2	Baltic Sea coast of Mecklenburg-Vorpommern	Teterow
3	North German lowlands western part, Lower Rhine area	Hamburg
4	North German lowlands eastern part	Berlin
5	Climate in rain shadow of the mountainous areas, eastern part	Magdeburg
6	Climate in rain shadow of the mountainous areas, western part	Frankfurt
7	Northern low mountain range areas	Bad Marienberg
8	Southern low mountain range areas	Nuernberg
9	Alps, higher locations of Black Forest and southern part of Bavarian Forest	Oberstdorf

Table 2: Soil Parameters for the "Synthetic" Surface Layer of All Soil Regions

Area	Depth [cm]	Sand [%]	Silt [%]	Clay [%]	OC [%]	OM [%]	FC [Vol%]	PWP [Vol%]	SAE	CAW
1	22.58	27.47	51.50	21.03	3.05	4.37	38.26	15.66	1	3
2	17.37	23.44	59.15	17.40	2.77	4.60	41.15	14.44	2	4
3	37.21	68.85	19.61	11.54	1.31	2.29	30.75	12.28	2	4
4	29.93	76.10	16.53	7.37	1.75	2.90	26.54	8.90	2	4
5	25.00	25.86	59.49	14.65	1.91	2.94	39.45	16.73	3	3
6	42.47	11.56	71.90	16.54	1.21	2.16	39.20	14.85	3	3
7	28.25	20.17	51.64	28.19	3.14	4.82	44.04	21.94	2	3
8	20.86	17.40	51.28	31.32	5.01	7.94	47.01	23.88	2	4
9	20.77	40.71	34.44	24.85	3.02	4.18	40.99	19.04	1	4
10	14.00	38.11	44.25	17.65	3.96	5.90	41.03	14.90	2	4
11	12.77	35.84	47.63	16.53	3.26	4.73	40.70	15.60	2	4
12	18.40	38.88	31.26	29.86	3.45	6.22	43.49	22.74	2	2-3

SAE = Susceptibility for Erosion (1 = low; 2 = middle; 3 = high; 4 = very high; CAW = Conductivity for Water (1 = very low; 2 = low; 3 = middle; 4 = middle to high; 5 = high; OC = Organic Carbon; OM = Organic Matter, FC = Field Capacity, PWP = Permanent Wilting Point (*8*)

The combination of 9 climate regions and 12 soil regions in Germany is the basis for establishing 22 leaching scenarios with different soil and/or climate characteristics each (Figure 6). The realistic worst case region used for modelling and outdoor lysimeter studies for the registration and admission of pesticides in Germany ("Borstel-Scenario") is similar to region No. 10, "Ancient Moraine Region (N.P.)".

The amounts of leachates compiled in Table 3 were computed (program PELMO, version 2.01) (*6*) based on these scenarios and for a period of 20 years. Simulations were carried out in parallel with three fictitious crop-protection products differing

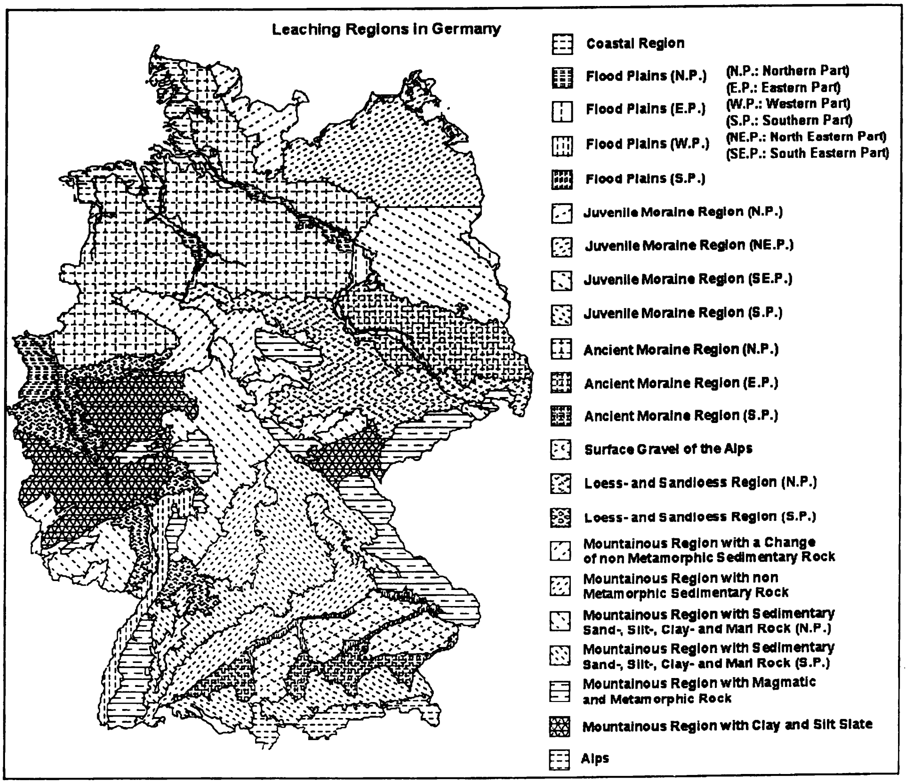

Leaching Regions in Germany
Coastal Region
Flood Plains (N.P.)
Flood Plains (E.P.)
Flood Plains (W.P.)
Flood Plains (S.P.)
(N.P.: Northern Part)
(E.P.: Eastern Part)
(W.P.: Western Part)
(S.P.: Southern Part)
(NE.P.: North Eastern Part)
(SE.P.: South Eastern Part)
Juvenile Moraine Region (N.P.)
Juvenile Moraine Region (NE.P.)
Juvenile Moraine Region (SE.P.)
Juvenile Moraine Region (S.P.)
Ancient Moraine Region (N.P.)
Ancient Moraine Region (E.P.)
Ancient Moraine Region (S.P.)
Surface Gravel of the Alps
Loess- and Sandloess Region (N.P.)
Loess- and Sandloess Region (S.P.)
Mountainous Region with a Change of non Metamorphic Sedimentary Rock
Mountainous Region with non Metamorphic Sedimentary Rock
Mountainous Region with Sedimentary Sand-, Silt-, Clay- and Marl Rock (N.P.)
Mountainous Region with Sedimentary Sand-, Silt-, Clay- and Marl Rock (S.P.)
Mountainous Region with Magmatic and Metamorphic Rock
Mountainous Region with Clay and Silt Slate
Alps

Figure 6: Leaching Scenarios in Germany.

with respect to sorption and biodegradation in soil (sorption coefficient related to organic carbon (K_{OC}): 60 ml/g, disappearance time for 50 % (DT_{50}): 15 d; K_{OC}: 150, DT_{50} 100 and K_{OC}: 400, DT_{50} 150). The crop selected for the simulation was winter wheat, the rate of application was 1.0 kg/ha annually applied in May. The concentrations of the three substances to be expected in the leachates annually are compiled in Table 3. The table elucidates possible regional differences concerning the leaching of organic substances in soil and consequently indicates simultaneously the potential risks for groundwater contaminations in the different regions.

Clarification on whether the selected scenarios are sufficiently representative for Germany or not needs further investigations.

Table 3: Calculated Groundwater Formation Rates and Average A.I. Concentrations

			Conc. of a.i. in µg/L in Leachate		
No.	Scenario	Amount of Leachate [L/m²]	a.i. with KOC 60; DT50 15	a.i. with KOC 150; DT50 100	a.i. with KOC 400 DT50 150
1	Coastal Region	195	< 0.000005	0.00054	< 0.000005
2	Flood Plains (N.P.)	161	< 0.000005	< 0.000005	< 0.000005
3	Flood Plains (E.P.)	57	< 0.000005	< 0.000005	< 0.000005
4	Flood Plains (W.P.)	54	< 0.000005	< 0.000005	< 0.000005
5	Flood Plains (S.P.)	61	< 0.000005	< 0.000005	< 0.000005
6	Juvenile Moraine Region (N.P.)	605	0.03129	11.62044	1.64035
7	Juvenile Moraine Region (NE.P.)	114	< 0.000005	0.79648	0.00005
8	Juvenile Moraine Region (SE.P.)	95	0.00002	3.08048	0.00991
9	Juvenile Moraine Region (S.P.)	78	0.00016	6.92819	0.06533
10	Ancient Moraine Region (N.P.)	243	0.00112	7.37429	0.34718
11	Ancient Moraine Region (E.P.)	10	0.00003	2.79243	0.00215
12	Ancient Moraine Region (S.P.)	82	0.00024	6.08815	0.01365
13	Surface Gravel of the Alps	63	0.00006	2.75308	0.02432
14	Loess and Sandloess Region (N.P.)	57	< 0.000005	< 0.000005	< 0.000005
15	Loess and Sandloess Region (S.P.)	61	< 0.000005	< 0.000005	< 0.000005
16	Mountainous Region with a change of non Metamorphic Sedimentary Rock and Loess	771	0.00002	0.51131	0.00733
17	Mountainous Region with non Metamorphic Sedimentary Rock	86	< 0.000005	0.00001	< 0.000005
18	Mountainous Region with Sedimentary Sand-, Silt-, Clay- and Marl Rock (N.P.)	771	0.00012	1.37950	0.05274
19	Mountainous Region with Sedimentary Sand-, Silt-, Clay- and Marl Rock (S.P.)	65	< 0.000005	0.04585	0.00001
20	Mountainous Region with Magmatic and Metamorphic Rock	771	0.04056	5.37909	0.84802
21	Mountainous Region with Clay and Silt Slate	771	0.05069	8.48578	1.73385
22	Alps	1332	0.05439	6.97027	1.35115

The calculated results for the "Borstel-Scenario" which is used in the registration and admission procedure for pesticides in Germany are given in Table 4.

Table 4: Groundwater Formation Rates and Average A.I. Concentrations for the "Borstel-Scenario"

Scenario	Amount of Leachate [L/m²]	Conc. of a.i. in µg/L in Leachate a.i. with KOC 60; DT50 15	a.i. with KOC 150; DT50 100	a.i. with KOC 400 DT50 150
Soil: Borstel / Climate: Hamburg	292	0.001	7.914	0.393

The results of the "Borstel-Scenario" are coincident with the results of leaching region No. 10, "Ancient Moraine Region (N.P.)", although the soil data for Borstel were derived from an existing site near Hannover and not averaged from soil maps. Figure 7 shows the spatial relationship between concentrations in leachates and leaching regions for a substance with a K_{OC} of 150 and a DT_{50} of 100.

Compared to the "Borstel-Scenario" higher concentrations of the a.i. in the leachate are partly simulated for leaching region No. 21, "Mountainous region with clay and silt slate", No. 22 "Alps" and No. 20 "Mountainous region with Magmatic and Metamorphic Rock" (e.g. for the a.i. with K_{OC} 400 and DT_{50} 150). This can be explained by very high amounts of precipitation. Concerning intensive agricultural use with intensively treated crops like winter wheat these regions are of minor interest due to their altitude and slope. However, the soil characteristics of soil region No. 3, "Juvenile Moraine region" indicate a lower sorption capacity for organic compounds compared to the "Borstel" soil, because the content of organic carbon is lower in all layers. In connection with a higher amount of precipitation (Hamburg 770 mm/year and Schleswig 880 mm/year) in leaching region No. 6, "Juvenile Moraine Region (N.P.)" the concentrations of all substances analysed are distinctly higher than in the "Borstel-Scenario". This leaching region therefore may be considered as a worst case region in Germany for the leaching of pesticides.

Conclusion

So far the potential of the lysimeter methodology for the general or site specific exposure/effects assessment is only used to a very limited extend. The examples given indicate possibilities for expansions of practical use resulting in reliable improvements of these assessments.

As regards the prediction of the sensitivity of regions from lysimeter data sets and Geographical Information Systems, a differentiation is possible. At present, this can only be comparatively used prior to further validation. Applications of the

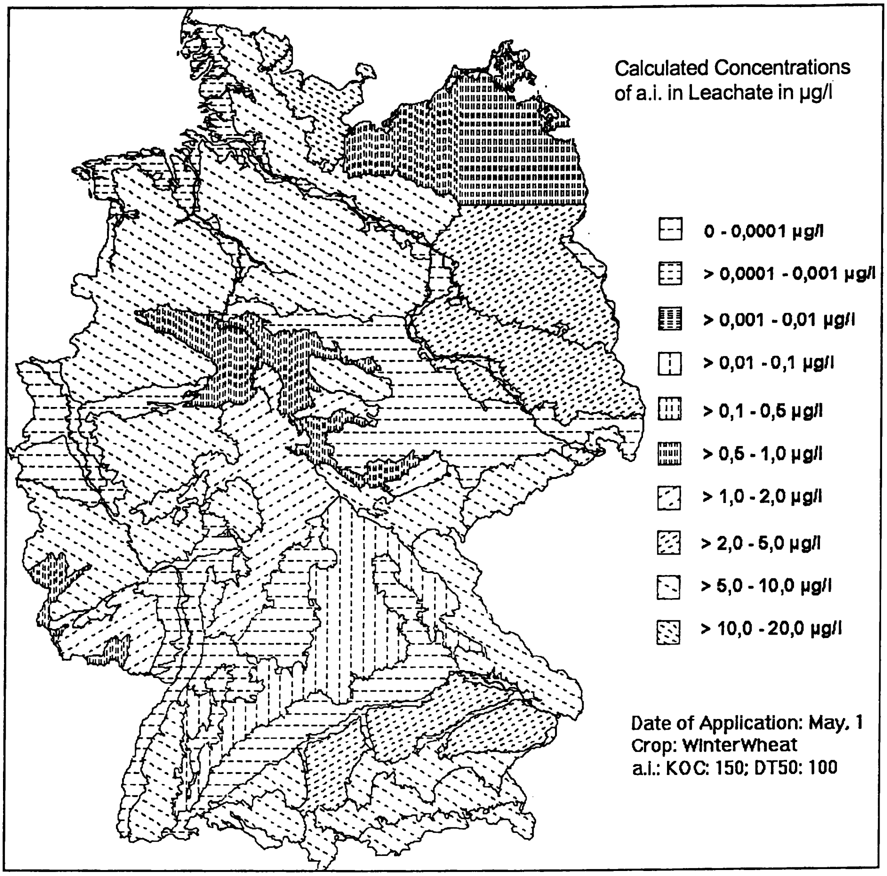

Calculated Concentrations of a.i. in Leachate in µg/l
0 - 0,0001 µg/l
> 0,0001 - 0,001 µg/l
> 0,001 - 0,01 µg/l
> 0,01 - 0,1 µg/l
> 0,1 - 0,5 µg/l
> 0,5 - 1,0 µg/l
> 1,0 - 2,0 µg/l
> 2,0 - 5,0 µg/l
> 5,0 - 10,0 µg/l
> 10,0 - 20,0 µg/l
Date of Application: May, 1
Crop: WinterWheat
a.i.: KOC: 150; DT50: 100

Figure 7: Calculated Average Concentrations in Leachates (a.i. K_{OC}:150 and DT_{50}: 100).

"regionalisation" may be to identify regions for monitoring and also to cross-check for assumptions within current assessment systems.

Acknowledgement

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Chapter 20

The Future of Pesticide Use: The Responsibility of Developed Nations Toward Lesser Developed Nations

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ABSTRACT The world's population doubled between 1950 and 1985. Nevertheless, through progress in agricultural science, increases in food production were achieved on an almost constant cultivated area. The predicted growth in world population to 6.1 billion by the year 2000 will continue to demand increases in food production on available agricultural land averaging only 0.2 ha per capita. Although pesticide use is a major contributor to stable crop yields, concern over consequences of injudicious pesticide use led to regulatory requirements for environmental fate data. The world pesticide market is dominated by about 10 corporations. Their intensive research and that of academic and government institutions in developed countries is essential to guarantee harvests. Developing countries must share benefits of pesticide development both to feed their populations and because their economic and social structures are influenced by the need to sell agricultural produce to richer countries. Consequently, developed countries have a moral obligation to adapt pesticide development to needs of Third World countries by providing them with appropriate testing techniques, assisting them to conduct environmental testing programs, and ensuring that data are obtained under relevant QA/QC and GLP procedures.

INTRODUCTION

Industrial and agricultural technologies are the basis of the wealth of richer countries. It is the responsibility of the richer countries to share or transfer agricultural technologies that will help developing countries to relieve malnutrition and starvation and raise living standards. This can only be achieved by a cooperation in which each partner commits appropriate resources.

In The Lysimeter Concept; Führ, F., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 1998.

Advances in agricultural technology have greatly benefited the richer nations of the world, but, in many developing or poorer nations whose economies are based on agricultural production, living standards have been slow to improve. On the other hand, the richer countries are able to purchase food and other agricultural products in a world wide market at relatively low prices. To sustain the balance of the world's food and trade system, it is important for the poorer countries to expand their agricultural production not only to feed their own populations, but also to provide sufficient for export revenue. It is desirable that this expansion takes place without adverse effects on natural resources and environment so that it is sustainable.

Transfer of technology is an important factor in correcting the imbalance between rich and poor nations. This paper addresses the special needs of the poorer countries and the obligations of the richer nations. The authors are well aware that many social, political, and economic factors also underlie the differences in wealth among the nations of the world but these are beyond the scope of this brief discussion. In this paper, we have attempted to summarize some of the complex issues involved in sharing the benefits of agricultural technology, specifically the use of chemical pest control methods. It represents the viewpoint of the authors and is based on their personal experience.

The richer countries have developed efficient agricultural systems that depend on high inputs of chemicals. Historical factors are important. Early in the nineteenth century, western Europe and the USA experienced the industrial revolution. Technological growth was rapid, as was the growth of institutions for the study of the applied sciences. The availability of financial capital for investment was also an important factor in establishing new enterprises. A mature chemical industry emerged which has continued to seek expanding markets for its products on an international basis.

The new industries had high labor requirements which led to rural depopulation and pressure to mechanize. Some benefits of modernization came late to agriculture such as the widespread introduction of chemical weedkillers at mid 20th century which helped to eliminate many backbreaking tasks that had kept many generations tied to the land.

Modern agricultural systems enjoy the support of a profitable agrochemical industry located at several major industrial centers in the USA, Western Europe and Asia where there are intellectual and material resources essential to the discovery, development of chemical technology and large-scale production of biologically active chemicals. The agrochemical industry has flourished by seeking global markets because the requirements of home markets could be rapidly met and the worldwide demand for agrochemicals grew as their potential benefits became manifest.

Poorer countries lack the capital resources and the infrastructure necessary for the costly enterprise of developing, testing and marketing new chemicals and often depend on small peasant farmers for production of food. Such countries have introduced the use of agrochemicals but, in addition to receiving benefits, adverse environmental effects and the development of resistant pest populations have often occurred as a result of poor management of the new technology. A major negative aspect of the rapid introduction of this unfamiliar technology was many, widespread incidents of human and animal poisoning.

The Food and Agriculture Organization of the UN (FAO), industry, and a variety of national and international organizations have attempted to ameliorate these problems by helping with the introduction of control measures and providing training in pesticide application, safe handling, determination of residues in food, disposal, etc. Such problems are global and these organizations have addressed problems common to all countries.

The "Safe Use Project " of the international pesticide manufacturers group (GCPF, formerly GIFAP) in Guatemala, Kenya and Thailand is an example of the commitment of the crop protection industry. This project has proven to be particularly effective in improving the understanding and application of crop protection through special education campaigns. Front-line programs were carried out in concerted actions involving the industry, national authorities, local government, the health service retailers, farmers and, especially, farm workers and their families. All those involved were made aware of the possibilities of modern technology and encouraged to use crop protection chemicals safely. This was no easy task in the lower social strata, where the rate of illiteracy is still very high. The results of the initiative speak for themselves, as the Thai example demonstrated. In Thailand more than half a million small scale farmers, farm workers, extension officers and rural doctors have been trained. This was only made possible by building up a pool of thousands of people as master trainers who were able to pass on the information in numerous courses.

Another important way to reduce residues is to search for active ingredients that control pest problems at a low application rates. Crop protection research efforts have achieved impressive successes in discovering such active ingredients: New products such as the pyrethroids, the azoles or the sulfonylureas are examples of such products. These active ingredients have set new yardsticks for the coming generations of products: Grams are used instead of kilograms.

Problems that are very specific to the locality or region, such as the persistence of residues on specific crops, worker re-entry into treated fields, potential for contamination of soil and water, may be very significant. At this point, the issue of responsibility becomes important. The manufacturer can provide instructions for safe use but it is important that a chain of responsibility be established that will involve the participation of the distributor, the purchaser and those who use the product to ensure that each understands the precautions necessary for using the product. A legal framework is also necessary. Much of the necessary environmental data must be obtained in the region where the product is to be used. Many studies to obtain these data are being undertaken in the developing countries through cooperative research that is supported by the richer countries, but more are needed.

POPULATION

The population of the world is increasing. The rate of increase in the developing countries will be greater than in the developed nations.

Predictions of future population, food needs, and agriculture rely on some basic assumptions. In this brief paper, it is sufficient to summarize the overall conclusions.

It has been estimated that the earth's population will reach 6 billion people by the end of the century and could reach 10 billion by 2050. A common estimate was that the earth's population will double in the next 100 years, but recent FAO projections indicate that the rate of growth is decreasing and that the population should plateau at 10.73 billion in 2071. The rate of growth between 1990 and 1995 was 1.48% per year, significantly lower than the 1.57% projected earlier[1]. The indications that the population may be stabilizing are welcome but differences in living standards between rich and poor nations remain a source of anxiety and potential instability.

In considering future food needs it is significant that, since 1985, the rate of increase of population in the developing countries exceeds that in the developed countries. Of the world's population growth of 80-90 million per year, Asia accounts for just under 60%, Europe 10%, Africa 12%, Latin America ca. 9%, North America 5% and the former Soviet Union ca. 5.5%. More than 50% of the world population in the developing countries is in the under-24 age group. This means that the rate of increase will not decline significantly in the near future.

Although the world's chronically hungry population has decreased to 840 million or 13.7% of the world's population from 920 million or 24.4% in 1974, currently, according to the World Food Program statistics, 11,000 children die each day from malnutrition. Political upheavals create major difficulties in food distribution and food aid levels from donor countries have decreased. Also, as a result of poor harvests and high prices, global food reserves are decreasing. Half of the world's hungry, or 420 millions live in Asia, although this number is expected to decrease. Sub-Saharan Africa remains one of the regions where the percentage of the population suffering from hunger, now 40%, has not decreased in recent years.

LAND AS A LIMITING RESOURCE

The world's acreage of arable land is limited (as are water resources). If food production is to meet the needs of growing populations, yield increases must be accompanied by reduction in losses due to pests.

Theoretically ca. 14 million km^2 of potential agricultural land remains available for food production but FAO expects that the losses due to urban development, desertification, poor cultivation methods, erosion, etc. will offset any increases from the use of new areas.

Assuming a world population of 6 billion by the year 2000, FAO estimates that, on an average, 0.2 ha of agricultural land will be available on a per capita basis[2].

The global situation gives an indication of future needs. However, food production and supply has become of less concern to the richer countries where the success of agricultural research in an industrialized economy has made it possible to achieve and sustain high production levels without continually increasing the area of land under cultivation.

The agricultural methods used in the 1960s provided yields that would require an additional 2.5 to 3 billion ha of arable land to sustain current production. This amounts to the combined areas of Europe, Brazil, and the USA (DLG figures)..

India and China currently contribute about 15 million yearly to the world's population. Provision of food, housing, education, and social needs places a substantial burden on these countries. China currently feeds its population on 7% of the world's agricultural area but to meet its future needs agricultural yields on existing areas must be increased by more than 3% per annum. According to official figures, China has produced 480 million tonnes of cereals in 1996. In the year 2030, this has to be increased to 640 million tonnes to feed the Chinese population which will then have reached 1.6 billion.

The richer countries have also become importers of agricultural products and contribute to the economies of the developing countries who provide raw materials, oil seeds, vegetable oils, vegetables, tropical fruits, etc.

Three types of cropping systems contribute to the general economy of the developing countries. Subsistence crops include traditional items of diet, such as cassava and millet. and often produce low yields because they are grown under conditions which do not allow them to reach their full genetic potential. Staple foods, such as potatoes, cereals, etc. are grown in the developed countries under conditions which afford close to optimum yield and quality. It has been difficult for developing countries to cultivate these crops efficiently, but this must be an important objective in achieving economic well being. Cash crops, such as cocoa, coffee, etc. are grown for export and contribute to the whole economy of the country. They may be unique and of high value. Unfortunately, the economies of developing countries suffer disproportionately owing to losses caused by pests.

Crop losses are substantial. On a worldwide basis during the years 1988-90, crop losses due to insects, weeds, and pathogens were 42.1% or $243.7 billion of a total production of $335.2 billion of eight principal cash and food crops (rice, wheat, barley, maize, potatoes, soybeans, cotton, and coffee). Most significantly, crop losses in those continents predominantly composed of developing countries were greatest: Africa 48.9%, Asia 47.1%, Latin America 41.3%, USSR 40.1%, Oceania 36.2% compared with 31.2% in N. America and 28.2% in Europe[3].

AGRICULTURAL PRODUCTION AND PESTICIDE USE

Pesticide consumption is growing in those developing countries which intend to improve the productivity of their agricultural systems. It is extremely important for them to establish functioning regulatory or monitoring systems.

Imports of pesticides to developing countries are rapidly increasing. However, some are now establishing an indigenous manufacturing industry through investment by the major multinationals or local enterprises. Vietnam provides a typical example of an importing nation which is rapidly becoming industrialized.

In Vietnam, 9.9 million hectares are used for agriculture and 7 million ha. or 21.2% of the country's total area are used for food crops. Rice is grown on 6.6 million ha., maize on 0.5 million ha., sweet potatoes 0.39 million ha., cassava 0.28 million ha., and sugarcane 0.15 million ha.

Recently, the economy of Vietnam has improved and there has been significant increase in food production. Rice production throughout Vietnam increased from 15.875 million tons in 1985 to 21.900 million tons in 1993. However, the increase in rice production has been accompanied by increases in pest infestation and disease. Infestations of brown planthopper, leafroller, stemborer, rice blast, and sheathblight have extended to larger areas and a number of new diseases have been noted over considerable areas, including bacterial yellow stripe (*Pseudomonas sp.*) (central Vietnam and the Red River Delta), tungro, and the twisted dwarf virus. Two new diseases have recently been reported: premature ripening and soft rot of stem.

Pest infestations are frequently responsible for serious yield losses and losses to pests and diseases were considerable and the average loss in the Red River Delta over the years 1988 to 1992 was 237,079 tons per year (equivalent in value to ca US $23 millions).

Chemical application is the major control method. An estimated 20,000 to 25,000 tons/year are used, (equivalent to 4,000 to 5,000 tons of active ingredient) in 3-4 applications yearly. This increases the cost of production, particularly to the disadvantage of the small farmer. Half the currently registered compounds (176) are organophosphates and chlorinated compounds, but there has been no assessment of adverse effects on food quality, producers, consumers, pesticide applicators, or the environment.

THE AGROCHEMICAL INDUSTRY

PESTICIDE DISCOVERY AND DEVELOPMENT. Only a limited number of multinational companies possess sufficient resources to develop a new chemical pesticide and bring it to the market.

Agriculture and the world's population at large derive substantial economic benefits from the use of pesticides. Not only have crop yields been maintained, but also the incidence of disease in man and domestic animals has been dramatically reduced, particularly in the tropics.

Innovative research and development is the most promising way to continuously improve the efficacy of crop protection products and thus benefit industry and sustainable agriculture. The search for new active ingredients becomes more difficult and expensive. Today, more than 40,000 new substances must be synthesized to provide a single new product. Nearly one third of the development costs are spent in toxicology and environmental fate studies to make certain that the new product is safe with regard to human health and the environment.

This represents a considerable investment by the agrochemical industry and there are now no more than 10 multinational industrial corporations capable of undertaking this enterprise[5]. There are many more manufacturers, distributors, and formulators worldwide who bring the products to the user, but they have inadequate resources for the development of a new compound and accumulation of the safety data that is required for its approval by US, European or Japanese authorities. At present, it costs about $100 - $200 million to bring a new active ingredient to the market. However, this investment sustains an industry that creates thousands of jobs throughout the world and agrochemical manufacturing and distributing companies are springing up in India, China, Korea, and other "developing countries".

It is important to bear in mind that the transfer of technology involves costs to its developer. Successful transfer requires cooperation and mutual agreement on goals with commitment of resources on both sides. It leads not only to direct benefits to agricultural production but also to the creation of jobs, training and educational programs, and improvement of the infrastructure. A background of political and economic stability is also a significant factor in nurturing and sustaining a new enterprise.

Pesticides are developed in the temperate countries. To achieve profitability, most pesticides are intended for major markets and are designed to control pests of major crops. In developing countries, data are needed relating to their use on unfamiliar crops and soils, under totally different climatic conditions envisaged during their initial development. Additional safety data may be required so registrants must balance the market potential against the cost of obtaining the data. If the result of the calculation is unfavorable the country concerned either loses a valuable chemical or the regulations must be relaxed in some way, thus placing officials in a difficult position.

TECHNICAL COOPERATION.

TECHNOLOGY TRANSFER. Technology transfer should be of lasting, mutual benefit to both the provider and the recipient. New agricultural technology must be adapted in an ongoing, hands-on process requiring continued cooperation and communication.

New agricultural technology will include higher yielding crops, better protection against pests and other stresses, better human and animal nutrition, and improved management systems. Besides genetic engineering of plants, fertilizers and pesticides are the major chemical inputs. New crop varieties will not only improve yields but by introducing resistance to various pests will increase the range of pest control measures. Fertilizers are essential if high crop yields are to be sustained. Pesticides are critically important for reducing losses during production and storage of food.

The individual standard of living in the richer countries has benefited by the decreasing proportion of family income which is needed to buy food. In Germany, only 17% of the average household income is now required for purchase of food as compared to 26% in 1971.

In this situation, the richer countries have been able to turn their attention to environmental issues. As developing countries strive to achieve economic self sufficiency, the role of agriculture is critical, not only for provision of food, but also for generating income at both national and farm levels. To achieve this, it is imperative that traditional agricultural systems be brought up to date.

When radical changes in technology are to be introduced, their potential impact should be carefully analyzed. Technology must be transferred with due regard to the locality in which it is to be used. It is important to learn from the lessons of the past. In the face of poverty and starvation, environmental questions become far less significant. Through primitive techniques of agriculture and wasteful exploitation, much agricultural land has been made unproductive so denying resources to future generations

Transfer of advanced agricultural techniques is rarely a simple matter. Agricultural production systems are specific to a region. Crops, soils, climate, terrain, and pests differ from location to location. Decisions to adopt or adapt new technology raise fundamental questions of culture and regional infrastructure.

An important component of the technology transfer process is an active agricultural research community that understands local needs. To flourish, it requires intensive communication and cooperation among academia, agriculture, industry, international organizations, and governments..

Pesticides are an essential component of modern large-scale agriculture and the agricultural community in the developed countries has had long experience of using pesticides in agricultural production systems. Their efficacy is well established and, before they can be marketed, stringent tests must be performed by the manufacturers to satisfy the regulatory authorities that they can be used safely and have no potentially adverse effects on the environment. A balanced view of their potential effects on the environment and the food supply is essential. The practice of agriculture brings about changes in the environment that affect the habitat of flora and fauna and the ecological consequences of pesticide use must be regarded in this context.

Although crop protection products may be extremely effective and friendly to the user- and to the environment, in the final analysis, it is the user who ensures that they are properly used so that they present no danger to the user, the environment, or the consumer. The increase in the incidence of human poisoning that occurred in China when organochlorine insecticides were replaced by organophosphate insecticides provides a good example of the consequences of adopting new technology in a society that has been insufficiently prepared by education to meet the change. The breakdown of chemical control of rice and cotton insect pests owing to the survival of resistant species provides a classical example of the failure of a technology that is adopted without proper safeguards.

There are many well-documented instances of the injudicious use of pesticides and trade practices, which led FAO to prepare a code of conduct[4] to provide guidelines for national and international trade in pesticides and prescriptions for their judicious use. The code was prepared in consultation with the Global Crop Protection Federation (GCPF formerly GIFAP).

Particular aims of the FAO code are to support countries that do not yet have their own legislation for registration, the promotion of fair commercial practices, and the promotion of procedures to ensure the safe use of crop protection products. Special emphasis is placed on collaboration between exporting and importing countries.

Paragraph 11 of the Code of Conduct states that: "The objectives of the Code are to set forth responsibilities and establish voluntary standards of conduct for all public and private entities engaged in or affecting the distribution of pesticides, particularly where there is no, or an inadequate, national law to regulate pesticides." Generally, poorer countries have adopted pesticide regulations but rarely possess capabilities for their enforcement. Economic constraints, lack of trained personnel, and, in some cases, corruption combine to bring about this state of affairs.

ANALYTICAL LABORATORIES. The developing countries require appropriate techniques to analyze pesticide chemicals before distribution and use, and residues in food and the environment.

The primary focus of government analytical laboratories, where they exist, is often the immediate task of determining residues in food and products for export. These laboratories are often faced with a variety of analytical tasks and lack effective quality assurance programs.

In the past, an important responsibility of government laboratories has been the determination of the amount of active ingredient in pesticide formulations and, in developing countries, the price and the quality of pesticide products are important, particularly when large stocks must be purchased through a bid process. The reputation of the manufacturer provides a guarantee as to the product, but this cannot be the sole guarantee because the number of pesticide suppliers has proliferated worldwide. Many of these are formulators and distributors and the ingredients of their products may originate from a variety of sources.

The FAO requires pesticides for plant protection needs and WHO requires pesticides for public health programs. To purchase stocks of pesticides internationally for their own use and to assist developing countries who might require specifications, the FAO and WHO convene a panel of invited experts who meet annually to prepare pesticide specifications. To support the specifications, Collaborative International Pesticides Analytical Council (CIPAC), in conjunction with representatives of the manufacturers, compile collaboratively studied methodology for analysis of active ingredients and determination of the properties of formulated pesticides. This analytical methodology is documented in a continuing series of handbooks.

Analytical residue methodology requires different techniques and validated methods may be proprietary in nature. National regulatory authorities, such as the USEPA, often act as repositories of validated residue analytical methodology. By ensuring the availability of appropriate and suitable methods for analysis of residues in food and environmental samples, the manufacturer provides an important component of the technology transfer process.

Residue analysis in developed countries may employ experimental techniques which are often inappropriate for routine use in many developing countries because they entail sophisticated instrumentation, highly trained operators, or expensive supplies There is an urgent need for inexpensive, reliable methods for screening pesticide residues. Currently, the FAO/IAEA Joint Division is evaluating the suitability of ELISA and TLC methods for this purpose.

To obtain data necessary to optimize pesticide use and safeguard the environment, many studies are being undertaken in the developing countries through cooperative research that is supported by the richer countries.

This is accomplished by the efforts of technical cooperation programs supported by international organizations (IAEA, FAO, etc.), national organizations (GTZ, etc.), and industry. Research and academic institutions in the developed countries also play an important role in staffing and implementing such projects.

As an example, The Institute of Radioagronomy has initiated lysimeter studies in Pakistan, Korea, Brazil, and India. The host institute at Julich ensured that the scientists involved were well briefed on the problem in hand and that experimental approaches were suitable. In addition, as a route to better mutual understanding of the issues, the institute acted to create a partnership between industry and the scientific community in the host country .

Technical cooperation and shared research efforts should confer benefits upon both donor and recipient. Additionally it should effectively pool knowledge and generate expertise in the region where the new technology is to be used:

Benefits of research

- minimizing crop losses and maximizing yields in developing countries
- optimizing application technology

- assessment and minimization of adverse environmental effects

Benefits of cooperation

- facilitates technology transfer by sharing costs and experiences
- shares cost of developing active ingredient
- shares cost of producing data on use of pesticides under environmental conditions at the location where the active ingredient will be used

Data obtained under temperate conditions, will provide a predictive framework that can be used to assess the potential behavior of these pesticide chemicals under tropical conditions. Such data and the use of models will no doubt be important in extrapolating behavior from one environment to another. However, there is a need for "real world" data. Mobility, volatility, and persistence may not be well predicted particularly with volcanic and lateritic soils that are common in the tropics, and this represents a major gap in current knowledge.

Agricultural research communities are aware of these deficiencies but official policies usually favor food production or health over what appear to be merely environmental issues. Although some aid agencies allocate resources to supporting research programs in a number of developing countries, the total is small in relation to the need.

A major obstacle to the international acceptance of data generated in developing country laboratories is the requirement that data be obtained in laboratories that meet the criteria of ISO guide 25 and operate under the OECD Principles of Good Laboratory Practices (GLP) or an equivalent requirement[6,7]. Until this is overcome there will be duplication of effort.

However, few laboratories in developing countries are in full compliance with GLP and major international efforts are needed to create an awareness of the need for compliance and the steps that must be taken to attain this goal. The Joint FAO/IAEA Division has just initiated a major program to assist laboratories achieve this objective.

There is an understandable tendency on the part of official agencies and industry to disregard studies that have not been conducted under GLP. However, it will be many years before most laboratories attain these standards and an important problem is to achieve intermediate stages of quality that will meet the need for credibility. There is a need for better understanding of the issues within the agricultural research community. Many sophisticated experimental systems have been used to study environmental processes in developing countries. To make use of this data represents a challenge to scientists and government authorities in countries where resources are scarce.

CONCLUSION

The world's population will continue to increase, whereas the earth's soil and water resources available for provision of food are finite. To provide food for increasing populations, yields on available land must be considerably increased in many developing countries. In response to these continuing challenges, new agricultural technology is continually being developed at the worlds major industrial and academic research centers. The needs are most acute in the developing countries where malnutrition and starvation are still commonplace. Here, it is imperative to step up production and reduce losses due to pests during production and after harvest.

Pesticide chemicals play a major role in pest management techniques and the effective transfer of this technology to the agricultural systems of developing countries is an important stage in assisting them to achieve economic self-sufficiency.

Regulatory safeguards are becoming more stringent and regulatory authorities impose needs for data that requires state-of-the-art research techniques. Uniform standards will promote international trade and protect human health and the environment. To conform, laboratories in developing countries must become capable of generating internationally acceptable data. The richer countries are cooperating by providing resources and performing research to obtain data on the environmental behavior of pesticides. However, there is still a great need for even more extensive efforts.

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